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ULTRA-MICRO CHEMICAL ANALYSIS

PART 3. POTENTIOMETRIC TITRATION

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GENERAL OBSERVATIONS

Until recently in carrying out volumetric determinations of a few micrograms of material one has had to work with rather dilute solutions, a method which is of course, open to a number of disadvantages [1]. Such small amounts of material can be determined with great accuracy if they are dealt with at the concentrations normally employed in macro-methods, by using correspondingly small volumes.

A method whereby this accuracy can be achieved is ultra-micro chemical analysis.

As indicated previously [2], all operations involving volumes of the order of 10^{-3} ml are carried out on the object stage of a microscope by means of manipulators which necessitate the use of specific apparatus.

Most published work on volumetric ultra-micro analysis is devoted to titrimetric determinations in volumes greater than 10^{-3} ml, in which microscope and manipulators are not used. Among work carried out along these lines, mention may be made of the work of I. M. Korenman and his coworkers [3,4]. They paid considerable attention to questions of the influence of the specific characteristics of ultra-micro volumetric analysis, and the consequent use of small volumes of test sample on the results of the determinations. A thiocyanate method [5] has been used for the micro-volumetric determination of silver in amounts of 2 – 15 μg. The use of the three basic methods of volumetric analysis (neutralization, oxidation-reduction, and precipitation) in ultra-micro methods is described in detail in the monograph by P. Kirk who systematized a large number of actual examples of various determinations [6].

Only one paper by A. Benedetti-Pikhler [1] is devoted to ultra-micro titration involving the use of microscope and manipulators. In this paper the final end point is determined by the color change of an indicator fixed on fine threads introduced into the solution.

Volumetric methods of ultra-micro analysis are used chiefly for the determination of the main components of very small samples of solid materials or solutions.

In view of the fact that the analytical principles of the ultra-micro method of chemical analysis do not differ from those of analysis of normal amounts of material [2], on switching over to ultra-micro chemical determinations, it is necessary to take into account all the data known about the reliability, advantages, and disadvantages of the method of analysis used. Thus errors arising during volumetric determinations involving the use of colored indicators, and also a number of technical errors are still pertinent when one

switches over to the ultra-microscopic scale; there are, however, a number of specific characteristics which must also be taken into account when working with micro-gram amounts of materials [3,6].

Potentiometric Ultra-Micro Titration

The use of electrometric methods for the determination of the end-point enables one to decrease, or even eliminate, drop errors and titration errors which are connected with the use of colored indicators. In this connection another advantage of physico-chemical methods becomes apparent; viz., that during electrometric titration it is possible to use dilute test and standard solutions. Great possibilities are opened up for ultra-micro analysis by the new method of high frequency titration which coes not require the introduction of electrodes into the cell.

Of electrometric methods of titration which are widely used at present, the most convenient method is potentiometric titration, since it enables changes in ionic concentration to be observed directly during titration. A number of difficulties which are consequences of dealing with small volumes hinder the application of potentiometric analysis in ultra-micro volumetric analysis. These difficulties, however, are not insuperable. Thanks to the advantages which electrometric determinations have over indicator methods of determining the end-points in ultra-micro analysis, the time has now come to develop methods for carrying out potentiometric titration on a micro scale. Though success has already been attained in this field without the application of the microscope [6,9], there is no published work on the technique (the use of microscope and manipulators) whereby such determinations can be carried out more conveniently by using manipulators for handling the small volumes involved.

Apparatus and techniques are described below for carrying out potentiometric titrations under the microscope.

a) Apparatus.

The basic apparatus by means of which all ultra-micro determinations [2] are carried out has to be modified slightly in oder to carry out potentiometric titrations. This is the result of having to use four manipulators instead of the usual two, because more instruments are involved in this particular technique. The additional manipulators are arranged on the same plate (Fig. 1).

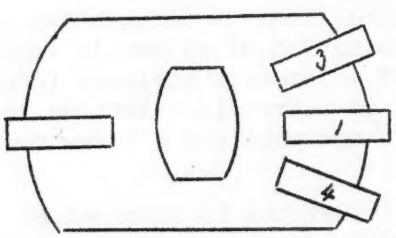

Fig. 1. The arrangement of manipulators during ultra-micro potentiometric determinations. 1, 2, 3, and 4 - manipulators.

The vessel in which potentiometric titration of small volumes is carried out is a small capillary (Fig. 2, a), 1 - 2 mm in diameter into which is fused a platinum wire b, one end of which serves as an electrode while the other end is connected via a mercury contact, c, and copper wire, d, to a potentiometer. The capillary is made in a micro-burner flame; the platinum wire is fused in and the capillary cut so that the working part of the capillary has an effective length of 3 - 4 mm. A drop of mercury is introduced into the opposite end of the capillary cut so that the working part of the capillary has an effective length of 3 - 4 mm. A drop of mercury is introduced into the opposite end of the capillary. The capillary is fixed with cement (3 parts rosin to 1 part paraffin wax) to one half of a piece of thick-walled capillary obtained by splitting the capillary along its axis. The glass holder with the capillary is fixed to the cover glass with the same cement.

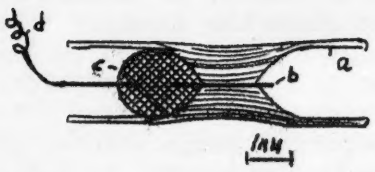

Fig. 2. Titration capillary. a - Capillary; b - platinum wire; c - mercury contact; d - connecting wire.

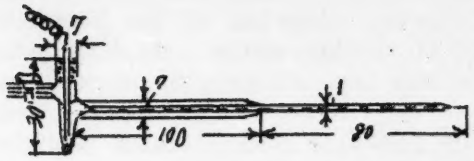

Fig. 3. The reference electrode.

A calomel electrode (Fig. 2) may be used as reference electrode, the working part of which is a fine capillary with a tip 0.05-0.1 mm in diameter. It is filled by placing a drop of mercury and calomel paste into the vertical part of the electrode and filling it with a solution of potassium chloride through the capillary tip by means of a water pump. The tip is then filled with a solution of potassium chloride and agar-agar.

Mixing of the solution, which is essential during titration, is most conveniently carried out when working with a microscope by using a stream of inert gas, which on impinging on the surface of the solution creates turbulent motion throughout the whole volume of the solution. The gas stream is led through an ordinary glass tube fitted with a tap; the end of the tube is drawn out into a capillary.

The buret used for introducing the titrant into the capillary is itself a capillary with a diameter of about 0.5 mm. The end of the capillary is drawn out to a diameter of about 20μ. The capillaries for making burets are prepared in the flame of a micro-blow pipe from thick walled tubes with an external diameter of 6 – 8 mm and an internal diameter of 2 – 4 mm. The shape of the cross section of the capillaries thus obtained is checked under the microscope, using for this purpose an ocular scale (in the vertical position) or a drop of mercury (in the horizontal position). The buret tips are drawn out in a quartz micro-

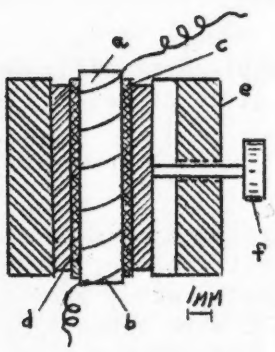

Fig. 4. Quartz micro-oven: a - quartz tube; b - nichrome winding; c - asbestos insulation; d - metallic body; e - metallic block for reinforcing the oven; f - clamping screw.

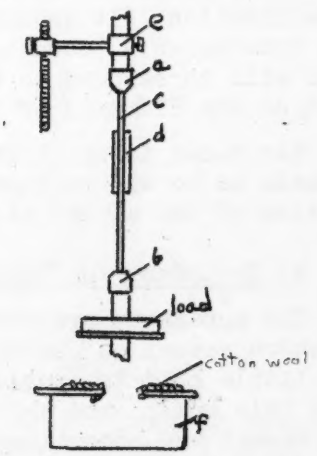

Fig. 5. Set-up for preparing microburets: a and b - clamps; c - capillary; d - quartz oven; e - reinforcement for the upper clamp; f - support.

oven (Fig. 4), which is connected to an AC supply through a rheostat and transformer (120 - 12 V). In order to draw out the tips thecapillarics are fixed in special clamps and fitted through the oven as shown in Fig. 5. That the internal diameter of the buret tip thus formed is correct is checked by means of an ocular scale. At that point of the buret where the diameter is the required one, an annular mark is made with a fine fibril of Canada balsam which has been heated beforehand. The buret is fixed in a micro-pipet holder [2], the opposite end of which serves for communicating with a leveling set-up (Fig. 6), which is used for creating pressure or rarefaction, respectively, counteracting or supporting the surface tension forces in the buret. In order to measure out a definite volume of titrant under these conditions, it is essential that the mark on the buret should be in the field of vision of the microscope. This is not always convenient. It is expedient, therefore, to use a buret constructed in the same way as the micro-pipet used in qualitative ultramicro analysis [2], but which enables the solution to be measured out accurately. For this purpose a pressure micrometer, b, is inserted in the piston apparatus between the holder, c, and the micro-screw, a, the movable part of the micrometer operating as a piston in the holder (Fig. 7). In such a buret a certain number of divisions read off

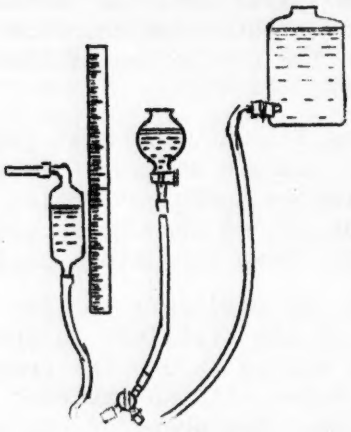

Fig. 6. Leveling assembly.

Fig. 7. Buret with pressure micrometer. a - Micro-screw; b - pressure micrometer; c - buret holder; d - buret.

by the needle on the micrometer dial for one turn of the screw corresponds to a definite volume of solution in the buret; this number is easily determined by calibration. It should be noted that the piston diameter should be cut down considerably (down to 1 mm); otherwise one scale division of the micrometer will correspond to too large a volume of solution expelled from the buret, so the accuracy of the reading is lowered.

The buret is calibrated by means of standard capillaries [1]; calculations are made as to what volume of liquid in a buret of given diameter does one scale division of the ocular micrometer correspond.

b) Procedure for Titration.

The apparatus prepared as described above is arranged as follows: the titration vessel is placed in a damp box on the object stage of a microscope (the little holders containing the titrant and reagents, etc., should also be in this box); the thick walled capillary with the wire connecting titration vessel and potentiometer is fixed in the left-hand manipulator; the micro-pipet (and subsequently the calibrated micro-buret) is fixed in the clamp of the right-hand manipulator; the reference electrode in the third manipulator; and the stirring device in the fourth.

The calomel electrode is introduced into the damp box with the help of the manipulator. While observing this under the microscope, the manipulator

rack is turned and a position is found for the tip of the calomel electrode such that it is arranged along the horizontal axis and is in the center of the field of vision. The titration vessel is then adjusted with respect to the tip of the calomel electrode until the electrode tip is in one half of the titration vessel. In this position, by observing with the naked eye, the wire connecting the titration cell to the potentiometer is fitted to the other end of the titration vessel by means of the left hand manipulator. In this way the mutual positions of the parts of the apparatus most difficult to coordinate are established. The only motions necessary to be made with the respective manipulators after establishing this position are then backwards and forwards.

With the left manipulator the end of the wire connecting titration vessel with the potentiometer is withdrawn, and the vessel itself is drawn back, thereby freeing the end of the calomel electrode, which is removed from the field of vision. The tip of the calomel electrode is then moved away to a certain distance and is arranged in a position parallel to its original position.

The titration vessel is now brought back into the field of vision arranging it so that its open end is almost at the opposite side of the field of vision along the center, and by observation through the microscope a position is found for the fourth manipulator such that the tip of the capillary which serves as the stirrer (the gas capillary) is brought up to the opening of the vessel and arranged along its axis. The manipulator used for handling the gas capillary is then pulled away, and the gas capillary fixed in a position parallel to that which it had under the microscope.

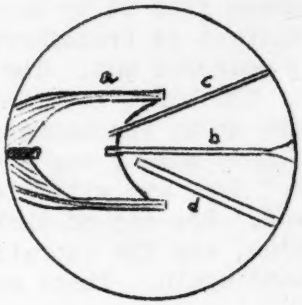

Fig. 8. Arrangement of the apparatus during titration (view under the microscope). a - Vessel; b - buret; c - calomel electrode; d - capillary for leading in the gas for stirring.

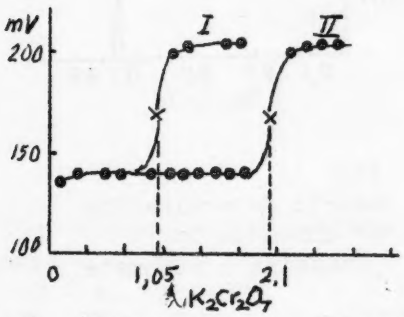

Fig. 9. Potentiometric determination of iron in Mohr's salt.
I - $1 \cdot 10^{-3}$ ml solution; II - $2 \cdot 10^{-3}$ ml solution.

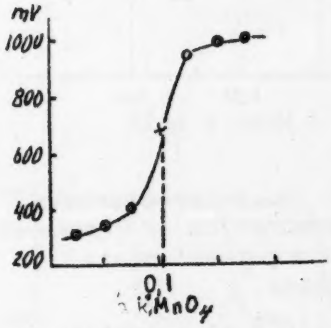

Fig. 10. Potentiometric determination of iron in Mohr's salt.

One of the vessels kept in the damp box in its holder is brought into the field of vision and filled with the solution to be titrated by means of the micro-pipet. From this vessel a known volume of solution is transferred to the titration vessel. Using the same micro-pipet after first having washed it out with water and the titrant, another vessel in the damp box is filled with titrant. Instead of this micro-pipet, the calibrated buret with the pressure is now fitted into the right hand manipulator. The tip of the calomel electrode is brought into the field of vision and arranged along the center. The titration flask is moved on to it until the tip of the electrode is in the solution. The opposite end of the titration flask is connected to the potentiometer. Measurements are made. Subsequently the above manipulations are repeated, and the connecting wire and the calomel electrodes are withdrawn. The vessel containing the titrant is now brought into the field of vision, and titrant is withdrawn from it by means of the buret which is evacuated by means of the piston. The titrant is transferred to the titration vessel, a definite volume of titrant being measured out. The amount is determined by the reading on the micrometer dial. The buret is withdrawn from the field of vision, and the gas capillary brought up to the titration vessel. The contents of the titration vessel are thoroughly mixed, the motion of the solution being observed under the microscope. They are withdrawn from the field of vision, and the gas capillary also removed. The tip of the calomel electrode is once more introduced into the solution, and the titration flask connected to the potentiometer. Measurements are made again. These manipulations are repeated until titration is complete.

The general arrangement of the apparatus during titration is shown in Fig. 8.

Titrations involving the use of a buret worked by means of a leveling device is carried out in exactly the same way, the only difference being that when adding a definite volume of titrant, the mark on the buret [1] is kept in the field of vision.

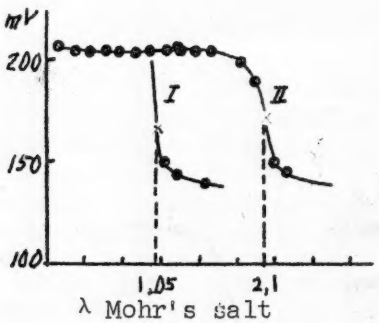

Fig. 11. Potentiometric determination of chromium in potassium bichromate.

I) $1 \cdot 10^{-3}$ ml solution;

II) $2 \cdot 10^{-3}$ ml solution.

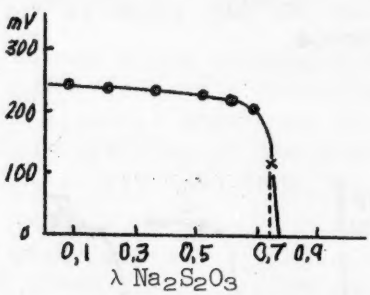

Fig. 12. Potentiometric determination of chromium in potassium bichromate.

TABLE 1

Determination of Iron in Mohr's Salt

Titrant Solution	Concentration in N	Amount used in ml	Solution of Mohr's salt titrated		Amount of iron in g		Error in %
			Volume in ml	Concentration in N	Taken	Found	
$K_2Cr_2O_7$	0.01	$1.99 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0.01	$1.12 \cdot 10^{-6}$	$1.11 \cdot 10^{-6}$	- 0.5
$K_2Cr_2O_7$	0.01	$1.01 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$0.56 \cdot 10^{-6}$	$0.566 \cdot 10^{-6}$	+ 1.0
$KMnO_4$	0.10	$0.102 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$0.56 \cdot 10^{-6}$	$0.57 \cdot 10^{-6}$	+ 2.0

TABLE 2

Determination of Chromium in Potassium Bichromate

Titrant Solution	Concentration in N	Amount used in ml	Solution of $K_2Cr_2O_7$ titrated		Amount of chromium in g		Error in %
			Volume in ml	Concentration in N	Taken	Found	
Mohr's salt	0.01	$1.98 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0.01	$3.46 \cdot 10^{-7}$	$3.43 \cdot 10^{-7}$	- 1.0
" "	0.01	$1.002 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$1.73 \cdot 10^{-7}$	$1.733 \cdot 10^{-7}$	+ 0.2
$Na_2S_2O_3$	0.10	$0.76 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$2.91 \cdot 10^{-6}$	$3.0 \cdot 10^{-6}$	+ 3.0

TABLE 3

Determination of Vanadium in Ammonium Vanadate

Titrant Solution	Concentration in N	Amount used in ml	Solution of NH_4VO_3 titrated		Amount of vanadium in g		Error in %
			Volume in ml	Concentration in N	Taken	Found	
Mohr's salt	0.01	$2.91 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	0.01	$1.53 \cdot 10^{-6}$	$1.48 \cdot 10^{-6}$	- 3.0
" "	0.01	$1.96 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0.01	$1.02 \cdot 10^{-6}$	$0.999 \cdot 10^{-6}$	- 2.0
" "	0.01	$1.023 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.01	$5.1 \cdot 10^{-7}$	$5.22 \cdot 10^{-7}$	+ 2.3

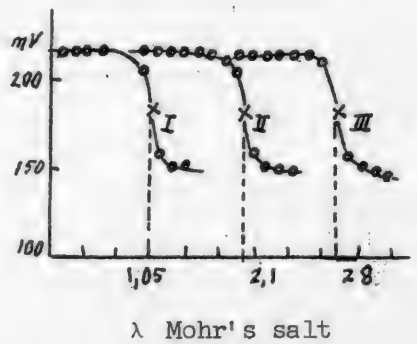

Fig. 13. Potentiometric determination of vanadium in ammonium vanadate. I - $1 \cdot 10^{-3}$ ml solution; II - $2 \cdot 10^{-3}$ ml solution; III - $3 \cdot 10^{-3}$ ml solution.

Potentiometric Ultra-micro Determination

Using the apparatus developed for ultra-micro titration, a number of determinations were carried out which demonstrated the possibilities of the method.

Solutions of known concentration were made in 5 ml standard flasks and aliquots taken. A PPT-1 potentiometer was used in conjunction with a galvanometer of sensitivity 10^{-8} A.

Results for determinations of iron in Mohr's salt, chromium in potassium bichromate, and vanadium in a sulfuric acid solution of ammonium vanadate are adduced in Tables 1, 2, and 3; the corresponding curves are given in Figs. 9, 10, 11, 12, and 13. A determination takes about 15 – 20 minutes.

SUMMARY

1. Apparatus and techniques have been worked out for potentiometric ultra-micro titration under the microscope.

2. Potentiometric ultra-micro determinations of 10^{-6} – 10^{-7} g of material in volumes of ca. 10^{-3} ml are described.

3. The results obtained are of a fairly high accuracy and their reproducibility is good.

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1) See Consultants Bureau Translation, page 377.

SPECTROGRAPHIC STUDY OF REACTIONS OF IMPORTANCE IN COLORIMETRY

I. COMPLEX COMPOUNDS FORMED BY NICKEL IONS WITH SODIUM-2-NITROSO-1-NAPHTHOL-4-SULFONATE

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1-Nitroso-2-naphthol and 2-nitroso-1-naphthol and their derivatives find wide use in colorimetric analysis for the determination of cobalt and other ions. We have already studied complex formation between cobalt and 1-nitroso-2-naphthol [1], and with sodium-1-nitroso-2-naphthol-3,6-disulfonate[nitroso-R-salt] [2], and also with other nitroso naphtholate derivatives.

In this paper we give results of our study of complex formation between nickel ions and sodium 2-nitroso-1-naphthol-4-sulfonate[nitroso-N-salt].

This compound was suggested by Sarver [3], as a qualitative reagent for cobalt. This reagent also gives colors with nickel, copper, and iron ions. No indications of the composition of the colored compounds formed are given in Sarver's paper, nor any information about their stability. Neither is there information on these points in articles published recently [4,5].

We prepared nitroso-N-salt by Witt and Kaufmann's method[1)] [6], and purified it by recrystallization from water. This was followed by washing with alcohol. Aqueous solutions of this reagent remain unchanged over long periods. All optical density measurements of the solutions were made with a spectrodensograph [7]. Hydrogen ion concentration was controlled by means of the quinhydrone electrode, in some cases with a glass electrode.

Fig. 1 illustrates absorption curves for solutions containing $6.21 \cdot 10^{-4}$ mol/liter nitroso-N-salt, and $2.07 \cdot 10^{-4}$ mol/liter nickel ions at various pH's.

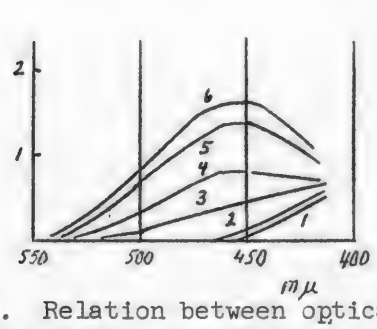

Fig. 1. Relation between optical density and pH. 1 - pH 2; 2 - pH 3; 3 - pH 4; 4 - pH 5; 5 - pH 6; 6 - pH 7-10.

Preliminary tests showed that the reaction between nickel and nitroso-N-salt practically finishes as soon as the solutions are mixed. The optical densities of solutions of constant pH but of different buffer mixtures differ from each other. As a result it was decided that in further work buffer mixtures would not be used and the pH would be adjusted by means of acid (HCl) or alkali (NaOH), the pH being controlled potentiometrically.

It is clear from Fig. 1 that on changing the pH from 2 to 10, the optical density, D, increases appreciably, tending to a limiting value. It is noteworthy that even at a pH of 10 no formation of nickel hydroxide occurs, although the nitroso-N-salt is not present in excess in this experiment. This testifies to the high stability of the colored complex.

1) For convenience nitroso-N-salt is abbreviated still further to RN.

In order to determine the stoichiometric coefficient in the equation for complex formation, we used Ostromyslensky's method [8] as modified by N. P. Komar [9]. Experiments were carried out at pH's of 4, 5, and 6. Measurements were made at λ = 450, 480, 500, and 520 mμ. The initial equimolar concentration of nickel ions and complexing agent was 8.27×10^{-4} in the first series, and 2.8×10^{-4} in the second series. Fig. 2 illustrates curves for ΔD composition of mixtures, where ΔD is the difference between the measured optical densities and the corresponding values for solutions of pure nitroso-N-salt for a given composition. We have only given results for one wave-length and for an initial concentration of $c_{Ni^{2+}} = c_{RN} = 8.27 \times 10^{-4}$ mol/liter. The thickness of the colored layer was $\underline{l}$ = 0.5 cm.

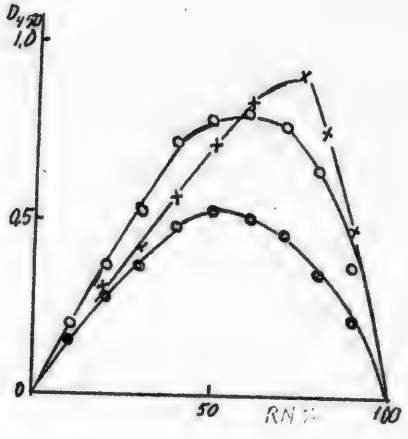

Fig. 2. Determination of composition:
-●-●- at pH 4;
-O-O- at pH 5;
-X-X- at pH 6.

The four series of tests at pH 4, two series at pH 5, and two series at pH 6 showed that the ratios of $c_{Ni^{2+}}:c_{RN}$ at the maximum of the curve ΔD-composition are respectively 1:1, 1:2 and 1:3. Further experiments were carried out along these lines at definite, fixed pH's.

First of all, the equilibrium at pH ≤ 4 was studied. Three series of tests were made at pH 3.5 by the method developed by Komar[10]. In all the experiments the ratios of the initial concentrations remained constant and equal to 1:1. The absolute value of the concentration varied from 4.14×10^{-4} to 1.65×10^{-4} mol/liter.

On the basis of the measured optical densities at λ=480 and 500 mμ, the molar absorption coefficients, ϵ_λ, were calculated by means of Komar's formula, which is suitable in cases of the formation of compounds with a composition of 1:1.

$$\epsilon_\lambda = \frac{1}{\underline{l}} \frac{D_i - nD_k}{c_i - nc_k}, \qquad (1)$$

where $\underline{l}$ is the thickness of the colored layer in cms; D_i and D_k are the optical densities of solutions with initial concentrations, c_i and c_k; and $n = \sqrt{\frac{D_i}{D_k}}$.

Statistically treated values of ϵ_λ are shown in columns 1 and 2 of Table 1. By means of these coefficients, equilibrium concentrations of the complex ($\underline{z}$ mols/liter) were calculated, and from these, the equilibrium constant of the complex formation reaction. In writing these reactions, one must initially take into account two possible variants of the equilibrium; in the first of these variants the following reactions are considered:

$$RN \rightleftarrows R^- + N^+ \qquad K_1; \qquad (2)$$

$$Ni^{2+} + R^- \rightleftarrows NiR^+ \qquad K_2 \qquad (3)$$

while in the second variant the following equation is also included:

$$Ni^{2+} + H_2O \rightleftarrows NiOH^- + H^+ \qquad (4)$$

In the first variant the overall process can be depicted by the equation:

$$Ni^{2+} + RN \leftrightarrows NiR^{+} + N^{+}, \quad (5)$$

for which

$$K_I = K_1 \cdot K'_2 = \frac{[NiR^+][N^+]}{[Ni^{2+}][RN]} = \frac{z}{(c-z)^2} \cdot h, \quad (6)$$

while in the second

$$Ni^{2+} + RN + H_2O \rightleftarrows NiRON + 2H^+, \quad (7)$$

for which

$$K_{II} = \frac{[NiRON][H^+]^2}{[Ni^{2+}][RN]} = \frac{z}{(c-z)^2} \cdot h^2, \quad (8)$$

where $z = [NiR^+]$ or $[NiRON]$, $c - z = [Ni^{2+}] = [RN]$, $h = [N^+]$, $c = c_{Ni^{2+}} = c_{RN}$. Calculations gave: $K_I = 0.74$ and $K_{II} = 2.30 \times 10^{-4}$. Results of statistical treatment of the mean value of K_I are adduced in Table 1, column 3.

TABLE 1

Results of the Statistical Treatment of Data Obtained during Calculations of the Molar Extinction Coefficients and Equilibrium Constants

Expt. No.	Calculated value	Mean value	No. of experiments, n	Dispersion S^2	Mean square error $S_{\bar{x}}$	t_α	$\pm t_\alpha S_{\bar{x}}$	Relative error, in %
1	ϵ_{490}	3240	21	1.7×10^{6}	287	2.09	596	18
2	ϵ_{500}	2800	21	1.3×10^{6}	252	2.09	530	19
3	K_I	0.74	26	1.7×10^{-2}	2.6×10^{-2}	2.06	5.4×10^{-2}	7
4	ϵ_{490}	3680	10	1.0×10^{4}	33	2.26	75	2
5	ϵ_{500}	2960	10	5.5×10^{4}	74	2.26	167	6
6	K_I	0.65	26	4.9×10^{-3}	1.2×10^{-2}	2.06	3×10^{-2}	4
7	ϵ_{500}	8650	20	3.1×10^{5}	124	2.09	260	3
8	ϵ_{510}	7370	20	4.9×10^{5}	156	2.09	330	5
9	K_{III}	3.63×10^{-5}	20	7.1×10^{-10}	5.9×10^{-6}	2.09	1.23×10^{-5}	33

Note. These results were treated by methods described in [12, 13]. Vide ibid. the significance of the symbols S^2, $S_{\bar{x}}$, t_α and $\pm t_\alpha S_{\bar{x}}$.

Formula (1) is the same for calculations of ϵ_λ at constant pH for both variants of the equilibrium, so that it is impossible to decide the question as to which of them corresponds to actual fact, (5) or (7), on the basis of calculations of ϵ_λ. In order to solve this problem, experiments were made at different pH values (within the limits 3.0 – 4.0) with mixtures of constant composition 1:1. In all the mixtures, $c_{Ni^{2+}} = c_{RN} = 8.27\times10^{-4}$ mols/liter. Optical densities ($D_{measured}$) were measured for different wave lengths. Using the molar extinction coefficients obtained earlier and the values of the constants K_I and K_{II}, the optical densities ($D_{calculated}$) were calculated for the same conditions; these were compared with $D_{measured}$. As shown in Fig. 3, $D_{calculated}$ follows changes in $D_{measured}$ satisfactorily only for the first variant of the equilibrium ($K_I = 0.74 \pm 0.05$). The fact that at a pH of 4 the hydrolysis of Ni^{2+} ions is completely insignificant, as can be easily calculated on the basis of the hydrolysis constant $K_3 = 5\times10^{-10}$ [11], is an indirect confirmation of this result.

A convincing proof of the existence of one complex of composition 1:1 at pH < 4 is given by experiments on the determination of ϵ_λ by the "saturation

method" in excess Ni^{2+} ions. Optical densities were measured for a wide wave length range at pH's of 3.3 and 3.8 for solutions containing various concentrations of RN and a constant concentration of Ni^{2+} ions which ensured a practically complete shift of equilibrium (5) to the side of the formation of the complex NiR^+.

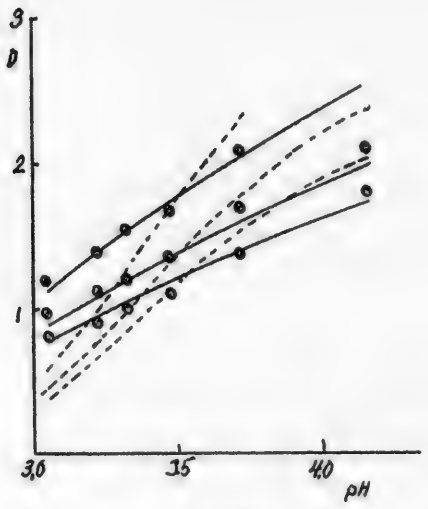

Fig. 3. Establishment of equilibrium type:
- - - calculated from K_{II} values;
——— calculated from K_I values;
● ● ● experimental values of D.

Corrections were applied to the values of D_λ for the characteristic color of Ni^{2+} ions, and ϵ_λ for the complex calculated on the basis of Beer's law. Columns 4 and 5 of Table 1 contain statistically treated mean values of $\bar{\epsilon}_\lambda$ for two wave lengths; they are similar to values of ϵ_λ obtained under equilibrium conditions (columns 1 and 2) and have a smaller error. We used these coefficients to calculate more reliable K_I values, the average value of which was: $\bar{K} = 0.65 \pm 0.03$. Statistically treated results are given in column 6, Table 1. "Saturation" experiments enable us to construct an absorption curve for a complex having a composition 1:1 (see Fig. 4, Curve 1).

In so far as $K_I = K_1 \cdot K'_2 = 0.65$ and $K_1 = 8.2 \times 10^{-7}$, then the constant of complex formation $K'_2 = 7.9 \times 10^5$, while the instability constant $K_2 = 1.3 \times 10^{-6}$.

Further experiments were made at pH $\geqslant$ 6. Under these conditions complex formation can be schematically represented by the equations:

$$RN \rightleftarrows R^- + N^+ \qquad K_1; \qquad (2)$$

$$Ni^{2+} + 3R^- \rightleftarrows NiR_3^- \qquad K'_4; \qquad (9)$$

or in general:

$$Ni^{2+} + 3RN \rightleftharpoons NiR_3^- + 3N^+ \qquad K_{III}, \qquad (10)$$

$$K_{III} = \frac{[NiR_3^-][N^+]^3}{[Ni^{2+}][RN]^3} = \frac{t \cdot h^3}{27(c-t)^4},$$

if $c_{RN} = 3c_{Ni^{2+}}$. Here $t = [NiR_3^-]$. In the case considered, formula (1) for calculation of ϵ_λ contains $n = \sqrt[4]{\frac{D_i}{D_k}}$.

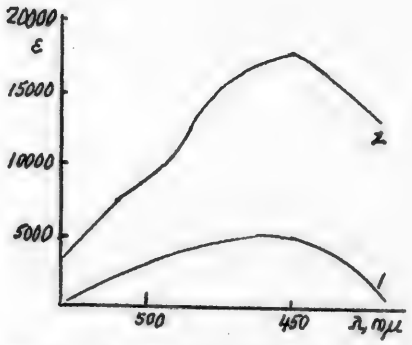

Fig. 4. Absorption curves:
1 - complex NiR^+, 2 - NiR_3^-

Two series of experiments were carried out at pH 6. In all the mixtures $c_{RN} = 3c_{Ni^{2+}}$. Optical densities were measured at $\lambda = 500$ and 510 mμ, and on the basis of these results, ϵ_λ was calculated first by means of formula (1), followed by calculation of K_{III}. Table 1 contains the results of statistical treatment of $\bar{\epsilon}_\lambda$ (columns 7 and 8) and K_{III} (column 9). $\bar{K}_{III} = (3.6 \pm 1.2) \times 10^{-5}$.

In so far as $K_{III} = K_1^3 \cdot K'_4 = 3.6 \times 10^{-5}$, while $K_1 = 8.2 \times 10^{-7}$, then $K_4 = 0.65$ while the instability constant $K'_4 = 1.5 \times 10^{-14}$.

The presence of two complexes with composition 1:1 and 1:3 complicates the use of simple methods of calculating for the determination of the properties of a possible complex with a composition of 1:2. The actual existence of this complex is in doubt since, in the presence of two other complexes, comparatively close to each other with respect to their optical results, the maximum observed on the Ostromyslensky-Job diagram at pH 5 may be a simple consequence of the superimposition of these two other complexes.

Let us assume that there are only two complexes of the composition 1:1 and 1:3 in the system under examination; then one can write the following equilibrium system:

$$Ni^{2+} + RN \rightleftarrows NiR^{+} + N^{+} \qquad K_I \qquad (5)$$

$$NiR^{+} + 2RN \rightleftarrows NiR_3^{-} + 2N^{+} \qquad K \qquad (11)$$

$$Ni^{2+} + 3RN \rightleftarrows NiR_3^{-} + 3N^{+} \qquad K_{III} \qquad (10)$$

from which

$$K = \frac{K_{III}}{K_I} = 5.6 \times 10^{-5} \qquad (12)$$

Here $[Ni^{2+}] = x$, $[RN] = y$, $[NiR^{+}] = z$, and $[NiR_3^{-}] = t$ are unknown, while $[N^{+}] = h$ is known. Four equations can be written:

$$zh = K_I xy; \qquad (13)$$

$$th^2 = Kzy^2; \qquad (14)$$

$$a = x + z + t; \qquad (15)$$

$$b = y + z + 3t, \qquad (16)$$

where $a = c_{Ni^{2+}}$, and $b = c_{RN}$

By substituting the values of z and t from equations (13) and (14) in equations (15) and (16), and making a simple transformation, we get the equation:

$$\frac{KK_I}{h^3} y^4 + \left(\frac{3aKK_I}{h^3} - \frac{KK_I b}{h^3} \right) y^3 + \frac{K_I}{h} y^2 + \left(1 + \frac{K_I a}{h} - \frac{K_I b}{h} \right) y - b = 0, \qquad (17)$$

by means of which it is possible to calculate $y = [RN]$, and therefrom all the remaining equilibrium concentrations.

Six mixtures were made up in which $c_{Ni^{2+}} = a = 2.07 \times 10^{-4}$ mol/liter, $c_{RN} = b = 6.21 \times 10^{-4}$ mol/liter, while the pH was varied from 2.0 to 7.0. Optical densities were measured at $\lambda = 500$ and 510 mμ. Using the known values of K_I, K, h, a and b, the coefficients of y in equation (17) were then calculated and from these the values of y, x, z, and t. Results of measurements and calculations are adduced in Table 2, while the corresponding graphs are given in Fig. 5. Knowing the equilibrium concentrations of the complexes and using the molar extinction coefficients obtained, it is not difficult to calculate the optical densities and compare them with the experimental values. Table 2 shows that the calculated values are in good agreement with measured ones, which testifies to the correctness of our assumption re the existence of only two complexes in the system under examination.

D_λ was measured in a wide wave length range for solutions of pH 7. From the values of D_λ found, optical densities d_λ corresponding to the absorption

TABLE 2

Results of Calculations of Equilibrium Concentrations in Relation to pH

$c_{Ni^{2+}} = a = 2.07 \times 10^{-4}$ mol/liter,

$c_{RN} = b = 6.21 \times 10^{-4}$ mol/liter.

Expt. No.	pH	[RN] y	$[Ni^{2+}]$ x	$[NiR^+]$ z	$[NiR_3^-]$ t	D_{500}		D_{510}	
						Calculated	Measured	Calculated	Measured
1	2.03	6.10×10^{-4}	1.99×10^{-4}	8.43×10^{-6}	2.02×10^{-12}	–	–	–	–
2	3.00	5.62×10^{-4}	1.52×10^{-4}	5.54×10^{-5}	9.73×10^{-10}	–	–	–	–
3	3.95	4.72×10^{-4}	5.56×10^{-5}	1.52×10^{-4}	1.44×10^{-7}	0.22	0.20	0.16	0.15
4	5.00	4.23×10^{-4}	6.64×10^{-6}	1.83×10^{-4}	1.79×10^{-5}	0.35	0.38	0.25	0.30
5	6.00	1.60×10^{-4}	8.16×10^{-7}	8.52×10^{-5}	1.21×10^{-4}	0.65	0.70	0.53	0.55
6	7.00	3.01×10^{-5}	1.66×10^{-7}	3.30×10^{-5}	1.73×10^{-4}	0.80	0.80	0.68	0.65

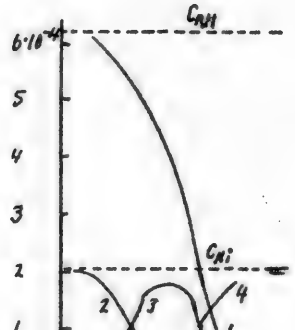

Fig. 5. Calculated equilibrium concentrations: 1 - [RN]; 2 - $[Ni^{2+}]$; 3 - $[NiR^+]$; 4 - $[NiR_3^-]$.

of complex NiR^+ were calculated, the concentration of the complex at this pH $[NiR^+] = 3.3 \times 10^{-5}$, while ϵ_λ values are adduced in Fig. 4. The difference $(D_\lambda - d_\lambda)$ is used for calculating ϵ_λ for the complex NiR_3^-. Results of calculations are adduced in the form of a graph (curve 2) in Fig. 4.

The complex NiR^+ is probably an ordinary inner-complex compound, in which the second valency of the Ni^{2+} ion remains in the ionized state. It is more difficult to decide this point for the somewhat unusual complex for bivalent nickel, NiR_3^- – whether it can be regarded as an inner complex compound. It may be that in this particular instance we are dealing with an acido-complex. We cannot completely reject the possibility of the formation of an actual inner complex compound, NiR_2. Experiment has only indicated that the concentration of such a complex, if there is one, does not exceed 3 – 4% of the total concentration of all particles in solution; i.e., it is within the limits of experimental error for the determination of optical density.

SUMMARY

1. It has been established that two complexes, NiR^+ and NiR_3^-, are formed in solutions containing Ni^{2+} ions and 2-nitroso-1-naphthol-4-sulfonate in accordance with the pH value.

2. The molar extinction coefficients of these complexes have been calculated, as well as their instability constants. For NiR^+, $K_2 = 1.3 \times 10^{-6}$, and for NiR_3^-, $K_4 = 1.5 \times 10^{-14}$.

3. The NiR_3^- complex is fairly stable in solution up to a pH of 10, and has high values for the molar extinction coefficients, which may be of interest for

the colorimetric and spectrophotometric determination of nickel.

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THE APPLICATION OF THE ULTRA-VIOLET IN ANALYTICAL CHEMISTRY

CERIMETRY IN THE ULTRA-VIOLET

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Solutions of quadrivalent cerium are known to possess a number of valuable properties [1, 2, 3] as compared with the widely used potassium permanganate: 1) acid solutions are very stable and maintain their normality over a long period, 2) they do not decompose on boiling for over an hour, 3) reduction proceeds without intermediate steps.

Determination of equivalence points during cerimetric titration in the ultra-violet is based on a sharp change in absorption at the transition $Ce^{IV} \rightarrow Ce^{III}$; quadrivalent cerium ions exhibit a very strong ultra-violet absorption at 356 $m\mu$, while trivalent cerium ions are completely transparent at this wave-length [4]. The method of determination does not differ from that used in previous work [5]. A more refined apparatus which we have constructed is used in this work instead of the ultra-chemiscope.

Having studied the conditions for determining the equivalence point in the ultra-violet of oxidation reduction reactions which are accompanied by the formation of compounds which are colorless in the ultra-violet, we came to the conclusion that the ultra-chemiscope could only be used when the material to be titrated has a very large absorption coefficient and very sharp absorption limits in the part of the spectrum used for absorption. The most suitable part of the spectrum for titration is at 365 $m\mu$ since ultra-violet rays of shorter wave length are absorbed by most chemical compounds. The use of an apparatus which gives ultra-violet rays of all wave lengths (including the short ones) for titration is, therefore, restricted. In the case of compounds which have diffuse absorption limits in the ultra-violet; i.e., those materials which, in addition to absorbing at λ = 365 $m\mu$, also absorb light of shorter wave lengths; a delayed onset of the titration end point is observed. On titration to darkening; i.e., to the appearance of absorption, the end point is observed sooner. Similar phenomena become apparent when fluorescent screens are excited not only by one particular band in the ultra-violet, but are also partially excited by others; e.g., uranium glass is excited by λ = 313 and 254 $m\mu$ as well as by λ = 365 $m\mu$.

It is known [6] that many compounds in solution, on irradiation with ultra-violet rays, undergo photo-chemical decomposition, and this may serve as an additional source of error during titration. As a rule the photo-reduction effect increases with increasing extinction coefficient and appears to be greatest at the maximum absorption of the ultra-violet [4]; i.e., to a greater extent in the short wave length region (313 - 254 $m\mu$). Thus the presence of short wave lengths in the pencil of rays isolated by an UFS-1 light filter of the ultra-chemiscope, increases photochemical decomposition which becomes observable with time (it becomes most apparent when titration of test material takes 5 - 10 minutes).

On carrying out an oxidation-reduction titration; e.g., of a solution of ferric chloride with ascorbic acid, hydrogen peroxide, cerium sulfate (IV), etc., we observed a premature (though with only a small deviation) onset of the titration end point, which could only be explained by photo-chemical reduction

of part of the solution being titrated.

In addition, the use of quartz cuvettes for titration also favors increased photo-reduction of the solution to be titrated as has been shown by Dain and Kachan [6], using the reduction of Ce^{IV} ions as an example. The quartz walls of the cuvette catalyzed photo-reduction considerably.

In order to achieve more accurate results, therefore, it is essential during titration to isolate that part of the spectrum to be used more monochromatically than can be done by means of the ultra-chemiscope; ultra-violet of $\lambda = 313$ mμ or less must be completely absent. The isolation of a particular part of the ultra-violet is of particular importance when there are other substances present which can absorb in the 313 – 254 mμ region.

We carried out titration, therefore, using the UFS-3 light filter which has maximum transmission at 365 mμ; i.e., at that part of the spectrum which is most useful for volumetric work. By using this light filter, we avoided errors arising from the absorption of shorter ultra-violet rays. Moreover the photo-chemical processes of reduction become practically insignificant since the absorption maxima of most of the substances participating in the reactions used for oxidation-reduction titration lie at wave lengths considerably shorter than 365 mμ. We also used ordinary chemical beakers instead of quartz cuvettes since practically no light of wave length $\lambda = 365$ mμ is absorbed by a thin layer of ordinary glass. With these modifications we got an apparatus which is extremely useful for volumetric analysis. All the examples of cerimetric titration described below were carried out with this apparatus.

Solutions of cerium sulfate (IV) in 1 N sulfuric acid were used in the present work. The scale divisions of the buret used were 0.005 ml.

EXPERIMENTAL

Titration of Oxalates with Cerium Sulfate (IV)

Cerium sulfate (IV) reacts with sodium oxalate as follows:

$$2Ce(SO_4)_2 + Na_2C_2O_4 = Ce_2(SO_4)_3 + 2CO_2 + Na_2SO_4.$$

The equivalence point is usually determined potentiometrically during cerimetric titration of oxalates. A visual method [7] is also known, but it is not easy to carry out since it requires preliminary preparation of ClI catalyst for speeding up the reaction, and also the presence of an indicator; the yellow color of cerium sulfate (IV) is not intense enough for fixing the end point.

TABLE 1

Amount of $C_2O_4^{2-}$ taken, in mg	Amount of $C_2O_4^{2-}$ found, in mg	Error, in mg
65.295	65.293	−0.002
65.295	65.299	+0.004

Titration in the ultra-violet permits the equivalence point to be determined visually without introducing catalyst or indicator. The determination is based on the difference in absorption in the ultra-violet at $\lambda = 365$ mμ of cerium sulfate (IV) and cerium sulfate (III). At the equivalence point a shadow appears on the screen which is a result of the presence of excess cerium sulfate (IV) in solution. The oxalate which is formed as the result of the reaction with sodium oxalate, and the sulfuric acid present in solution do not absorb in the ultra-violet at this wave length [8]. The solution of oxalate to be titrated is heated beforehand to 90° and 5 ml of sulfuric acid (1:5) added to prevent precipitation of cerium sulfate. Results of titrations are given in Table 1.

It is evident from the table that the experimental error is very small. The method can be used for preparing standard solutions of cerium sulfate (IV).

Titration of Antimony Trichloride with Cerium Sulfate (IV)

Cerium sulfate (IV) reacts with antimony trichloride according to the equation:

$$Ce(SO_4)_2 + SbCl_3 + 2HCl = Ce_2(SO_4)_3 + SbCl_5 + H_2SO_4.$$

Willard and Young [2] used this reaction for electrometric titration. Rathsburg [9] has checked on the possibility of a visual titration of antimony trichloride with cerium sulfate (IV); he used methylene blue, methyl orange, and methyl red as indicators.

We checked the titration of antimony trichloride with cerium sulfate (IV) in the ultra-violet. We showed that the reaction between antimony trichloride and cerium sulfate (IV) only follows the above equation when both solutions to be titrated are 1 N with respect to sulfuric acid. In this case the reaction is rapid and the end point is easily fixed by the appearance of a shadow on the luminescent screen. When the concentration of sulfuric acid is high, the solution starts to absorb the ultra-violet immediately after the addition of a few drops of cerium sulfate (IV) to the antimony trichloride. It is probable that the antimony chloride formed as the result of the reaction forms a compound with sulfuric acid in strongly acid media which absorbs the ultra-violet at 365 mμ. Hydrochloric acid in any concentration does not interfere with the antimony determination. Titration results are given in Table 2.

TABLE 2

Sb taken, in mg	Sb found, in mg	Error, in mg
25.437	25.420	− 0.017
25.437	25.417	− 0.020

Titration of Sodium Arsenite with Cerium Sulfate (IV)

The following reaction lies at the basis of the interaction between sodium arsenite and cerium sulfate (IV):

$$Ce(SO_4)_2 + Na_3AsO_3 + H_2O = Ce(SO_4)_3 + Na_3AsO_4 + H_2SO_4.$$

Willard and Young [2] carried out a visual determination of sodium arsenite with cerium sulfate (IV) in the visible spectrum using ClI as a catalyst and methylene blue as indicator.

Titration in the ultra-violet was carried out as follows: the arsenite solution was heated to 90°, and to the hot solution was added a solution of cerium sulfate (IV) until a shadow appeared on the luminescent screen, indicating the end point. Titration results are adduced in Table 3.

TABLE 3

As taken, in mg	As found, in mg	Error, in mg
16.094	16.074	− 0.020
16.094	16.078	− 0.016

Titration of Stannous Chloride with Cerium Sulfate (IV)

The most frequently used volumetric method of determining stannous chloride is the iodometric method. Nevertheless because of the volatility of iodine, titration in the presence of starch, and the easy oxidizability of stannous chloride by atmospheric oxygen, the errors of this method are considerable.

TABLE 4

Sn taken, in mg	Sn found, in mg	Error in mg
28.766	28.736	− 0.030
28.766	28.732	− 0.034

Colorimetric titration of stannous chloride in the ultra-violet eliminates the first two sources of error: the working solution is a stable solution of cerium sulfate (IV), while the end point is indicated by absorption of the ultra-violet by the solution as the result of the appearance of excess cerium sulfate

(IV). Oxidation by atmospheric oxygen can be avoided by carrying out the titration of stannous chloride in a carbon dioxide atmosphere.

Stannous chloride and cerium sulfate (IV) react in acid media as follows:

$$2Ce(SO_4)_2 + SnCl_2 + 2HCl = Ce_2(SO_4)_3 + SnCl_4 + H_2SO_4.$$

Hydrochloric and sulfuric acids as well as $SnCl_2$ and $SnCl_4$ are transparent to the ultra-violet at the wave length employed in titration (365 mμ). Absorption, as in previous examples, is solely shown by cerium sulfate (IV). Titration results are given in Table 4.

Titration of $SnCl_2$ and Na_3AsO_3 When Both Are Present Together

Determination of $SnCl_2$ and Na_3AsO_3 when present together is possible on the following grounds: the normal oxidation potential of the system $Ce^{IV} + e \rightleftharpoons Ce^{III}$ is + 1.55 V; of the system $Sn^{II} - 2e \rightleftharpoons Sn^{IV}$ is + 1.54 V; and of the system $H_3AsO_3 + H_2O - 2e \rightleftharpoons H_3AsO_4 + 2H^+$, + 0.574 V. Accordingly stannous chloride will be first titrated in solution, followed by the arsenite, since the potential difference between cerium sulfate (IV) and stannous chloride is considerably greater than that between cerium sulfate (IV) and arsenite. Arsenite is only titrated on heating the solution to 90°.

In order to determine $SnCl_2$ and Na_3AsO_3 when they are present side by side in the solution to be titrated, a small piece of marble is introduced into the solution and cerium sulfate (IV) is added dropwise until a shadow falls on the luminescent screen. The mixture is then heated to 90°, and cerium sulfate (IV) again is added until a second shadow appears. The number of mls of cerium sulfate (IV) used to titrate to the first end point corresponds to the amount of $SnCl_2$ in solution, while the number of mls of cerium sulfate used to get the second end point corresponds to the amount of arsenite. Titration results are given in Table 5.

TABLE 5

Sn taken, in mg	Sn found, in mg	Error, in mg	As taken, in mg	As found, in mg	Error, in mg
28.766	28.732	− 0.034	16.094	16.074	− 0.020
28.766	28.734	− 0.032	16.094	16.072	− 0.022

These results show that the accuracy of the determination of tin and arsenic when present together is the same as when they are determined independently.

Titration of Sulfite with Cerium Sulfate

Sulfites are normally determined in the visible spectrum iodometrically. The same drawbacks apply in this case as in the iodometric determination of tin. The errors are eliminated on using ultra-violet titration.

TABLE 6

SO_3^{2-} taken, in mg	SO_3^{2-} found, in mg	Error, in mg
17.962	17.972	+ 0.010
17.962	17.970	+ 0.008

Cerium sulfate (IV) can react with sulfite in two ways [10]:

1. $2Ce(SO_4)_2 + Na_2SO_3 + H_2O = Ce_2(SO_4)_3 + Na_2SO_4 + H_2SO_4.$

2. $2Ce(SO_4)_2 + 2Na_2SO_3 = Ce_2(SO_4)_3 + Na_2SO_4 + Na_2S_2O_6.$

On carrying out some tests, it became clear that in order to titrate sulfite completely, an amount of cerium is required which corresponds to the sum of these two reactions:

$$4Ce(SO_4)_2 + 3Na_2SO_3 + H_2O = 2Ce_2(SO_4)_3 + 2Na_2SO_4 + Na_2S_2O_6 + H_2SO_4.$$

In this case 1 ml of 0.1 N cerium sulfate corresponds to 0.050089 g of sulfite.

The end point, as in previous examples, is established by the appearance of shadow on the luminescent screen. During titration a small piece of marble is placed in the solution in order to avoid atmospheric oxidation. Results are given in Table 6.

Titration of Thiosulfate with Cerium Sulfate (IV)

When a solution of cerium sulfate (IV) is added rapidly to thiosulfate, the reaction which proceeds as follows occurs:

$$2Ce(SO_4)_2 + 2Na_2S_2O_3 + H_2SO_4 = Ce_2(SO_4)_3 + 2Na_2SO_4 + 3SO_2 + H_2S.$$

The end point is established by means of potassium iodide which acts as an ultra-violet indicator for the titration. Determination is carried out as follows: To the solution to be titrated is added 2-3 drops of 5% potassium iodide and titration carried out rapidly with cerium sulfate (IV) until the ultra-violet "color" of free iodine appears at the equivalence point. Titration results are given in Table 7.

TABLE 7

$S_2O_3^{2-}$ taken, in mg	$S_2O_3^{2-}$ found, in mg	Error, in mg
52.390	52.400	+ 0.010
52.390	52.395	+ 0.005

TABLE 8

Ce taken, in mg	Ce found, in mg	Error, in mg
135.010	133.600	+ 1.410
135.010	134.100	- 0.910

Titration can be carried out in reverse — cerium sulfate (IV) with thiosulfate. In this case potassium iodide is added to the solution of cerium sulfate to be titrated until all the iodine which separates out has dissolved completely, and the titration carried out with thiosulfate. In this case the error of determination increases somewhat because of the volatility of iodine (Table 8).

Titration of Potassium Thiocyanate with Cerium Sulfate (IV)

Potassium thiocyanate reacts with cerium sulfate (IV) according to the following equation:

$$6Ce(SO_4)_2 + KSCN + 4H_2O = 3Ce_2(SO_4)_3 + KCN + 4H_2SO_4.$$

The indicator for this titration in the ultra-violet, as before, is absorption of the ultra-violet by cerium sulfate (IV). Potassium thiocyanate does not absorb the ultra-violet at the operating wave length [11]. Titration is carried out as already described. Results are given in Table 9.

TABLE 9

SCN^- taken, in mg	SCN^- found, in mg	Error, in mg
2.397	2.390	- 0.007
2.397	2.387	- 0.010

Titration of Iodides with Cerium Sulfate

Willard and Young [2] established by potentiometric titration that the reaction between cerium sulfate (IV) and iodide quantitatively follows the equation:

$$2Ce(SO_4)_2 + 2KI = Ce_2(SO_4)_3 + I_2 + K_2SO_4.$$

We used this process for iodide determination in the ultra-violet. To the solution of potassium iodide to be titrated is added excess cerium sulfate (IV) until the iodide is completely oxidized, then 5-10 ml of 30% ammonium fluoride are added to combine with residual cerium sulfate (IV). The iodine is then titrated with thiosulfate to complete disappearance of the shadow on the fluor-

escent screen.[1] Results are given in Table 10.

TABLE 10

I taken, in mg	I found, in mg	Error, in mg
13.327	13.290	− 0.037
13.327	13.385	+ 0.058

TABLE 11

Pb taken, in mg	Pb found, in mg	Error, in mg
102.740	102.730	− 0.010
98.200	98.185	− 0.015

Titration of Solutions of Salts of Strontium, Calcium, Cadmium, Silver, and Lead with Cerium Sulfate (IV).

Because ions of strontium, calcium, cadmium, silver and lead do not act as reducing agents and do not react directly with Ce^{IV} ions, we worked out an indirect method for the determination of the metals mentioned using cerium sulfate (IV). The procedure adopted was as follows: to the solution of the metal salt to be titrated was added a known excess of standard sodium oxalate. The precipitate formed was filtered off, and the residual oxalic acid determined in an aliquot of the filtrate by titration with cerium sulfate (IV) in the ultraviolet using the method described above. The amount of metallic ion is then calculated by means of the following equations:

$$Me + C_2O_4^{2-} = \downarrow MeC_2O_4;$$
$$2Ce^{IV} + C_2O_4^{2-} = 2Ce^{III} + 2CO_2.$$

The mean experimental error for all the metals mentioned above does not exceed ±0.015 mg. Examples of results obtained with lead are adduced in Table 11.

ANALYSES OF LEAD ALLOYS

In order to check this cerimetric method in the ultra-violet, we used two alloys of the "Pripoi" type. A semi-quantitative spectrographic analysis was first made of the alloys in order to verify whether there are any elements present which may interfere with lead and tin determinations. As can be seen from the analytical results (Table 12), the elements which are present are present in amounts which will not interfere with the determination of tin and lead.

TABLE 12

Element	Alloy I	Alloy II	Element	Alloy I	Alloy II
	Amount in %			Amount in %	
Pb	Very high	Very high	Mg	0.001	0.001
Sn	—	Very high	Ca	—	0.001
Bi	0.01	0.01	Fe	0.01	0.001
Sb	—	0.01	Ni	—	0.001
Ag	0.001	0.01	Cu	0.01	0.001
Si	0.0001	0.0001			

Analysis of Alloy I

Determination of Lead. Results of gravimetric determination of lead by Dymov's method [12] are given in Table 13.

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[1]) In view of the fact that on addition of ammonium fluoride to combine with excess cerium (IV), a precipitate of cerium fluoride is formed, it is recommended that a minimal excess of cerium be used.

Method of Determination in the Ultra-Violet. Ca. 0.1 g of alloy was dissolved in 15 ml nitric acid (1:1). The solution was diluted with water to 100 ml and neutralized to the methyl orange end point. To the neutral solution was added a drop of 78% acetic acid to get rid of turbidity. The solution was then evaporated to 10-15 ml and excess oxalic acid added. Residual oxalic acid was determined in the filtrate by titration with cerium sulfate (IV) and the amount of lead calculated from the results. Results are given in Table 14.

TABLE 13

Weight of $PbSO_4$, in g	Weight of Pb, in g	Pb, in %
0.1429	0.09779	97.79
0.1432	0.09783	97.83

TABLE 14

Aliquot, in g	Weight of Pb found, in g	Pb, in %
0.1000	0.09822	98.22
0.1000	0.09803	98.03

Analysis of Alloy II

1) Determination of Tin. Tin was determined first gravimetrically by Dymov's method [12]. Results are given in Table 15.

These results are in good agreement with those obtained by cerimetric titration of tin in the ultra-violet; the latter was carried out as follows: ca. 0.1 g of alloy was dissolved in 30 ml of concentrated hydrochloric acid. To the solution obtained were added small pieces of marble, and stannous chloride titrated with cerium sulfate (IV) in the ultra-violet. Results are given in Table 16.

TABLE 15

Weight of SnO_2, in g	Weight of Sn, in g	Sn, in %
0.2010	0.1583	31.66
0.2008	0.1576	31.52

TABLE 16

Aliquot, in g	Weight of Sn found, in g	Sn, in %
0.1000	0.03159	31.59
0.1000	0.03159	31.59

2) Determination of Lead. After precipitation of the metastannic acid, lead was determined in the residual filtrate both gravimetrically and volumetrically by the methods already described. Gravimetric and volumetric results are given in Table 17.

TABLE 17

Gravimetric Method			Volumetric Method		
Weight of $PbSO_4$, in g	Weight of Pb, in g	Pb, in %	Aliquot, in g	Weight of Pb found, in g	Pb, in %
0.09920	0.06773	67.73	0.1	0.06807	68.07
0.09940	0.06781	67.81	0.1	0.06813	68.13

These examples show that cerimetric determinations in the ultra-violet are just as accurate as the method normally used in the visible part of the spectrum.

G. Z. Ileva carried out some of the experimental work.

In conclusion I should like to thank Prof. Yu. V. Morachevsky for his continuous help in carrying out this work.

SUMMARY

1. The principles of cerimetric determination in the ultra-violet are described.

2. The limitations of the ultra-chemiscope for analytical purposes are discussed and a new apparatus is described by means of which titration can be

carried out in the ultra-violet.

3. Cerimetric determinations are described for antimony, tin, strontium, calcium, cadmium, silver and lead; a method is described for the cerimetric determination of tin and arsenic when they are present together.

4. Cerimetric methods are described for oxalates, sulfites, arsenites, thiosulfate, thiocyanates, and iodides.

5. The analysis of lead alloys by a cerimetric method in the ultra-violet is described.

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PHOTOCOLORIMETRIC DETERMINATION OF ANTIMONY IN ORES BY AN IODIDE-THIOUREA METHOD

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A method for the routine determination of antimony in ores which is convenient and rapid is that based on the formation of the greenish-yellow iodide-antimony complex. In order to deal with the iodine which is evolved during the formation of this complex, it is essential to add a reducing agent. Of a number of materials which we tested for this purpose, the most suitable proved to be thiourea; it differs from sulfurous acid and bivalent tin in that it does not form colored compounds in a sulfuric acid medium with either iodide or antimony.

In addition, thiourea eliminates interference from a number of other elements by combining with them to form colorless, soluble complexes [1-3]. This property has been used for the determination of antimony without preliminary removal of copper, iron, mercury, tin, and arsenic. In particular, the cuprous thiourea complex is so stable that even at molar concentrations of copper and iodide, no precipitate of cuprous iodide is formed if sufficient thiourea is present; nickel and cobalt do not interfere either as long as their amounts do not exceed 5-10 mg in 50 ml solution.

In addition to ions which interfere because of their characteristic color (large amounts of Ni^{2+}, Co^{2+}, Cr^{3+}), bismuth should also be completely absent, since, under the experimental conditions used, bismuth gives a colored complex whose color is 4 – 5 times more intense than the one formed by antimony.

The presence of more than 0.5% chloride leads to a weakening of the color because of the conversion of antimony to the colorless chloride complex. Nitrates and sulfates of the alkali metals, ammonium nitrate, and sulfate, as well as tartrates in the concentration range 0.2 – 2 N do not affect the optical density of the solution.

The very low stability of the iodide-antimony complex in aqueous media necessitates the use of a large excess of potassium iodide. Thus, in order to develop an initial color threshold (E = 0.01) at an antimony concentration of 0.0001 M, a 30-fold excess of iodide must be used, and on dilution of the solution to be determined colorimetrically 10 times, a 750-fold excess of iodide is necessary. The complex is more stable in diethyl ether media, by which it is readily extracted, but even in this case, not less than a 3-fold excess is necessary in comparison with the calculated amount required for formation of $HSbI_4$.

We used the following optimal reagent concentrations: 7.5 g H_2SO_4, 1.5 g KI and 0.1 g $CS(NH_2)_2$ in 50 ml solution.

The graphs in Figs. 1 and 2 show that the optical density of the solution increases with sulfuric acid and potassium iodide concentrations, but it does not increase steadily. A deviation of ± 15-20% in the acidity does not lead to significant changes in optical density; the complex behaves similarly in nitric acid. At the concentration of sulfuric acid employed, up to 0.4 N nitric acid can be present. With deviations of ±10% in the concentration of iodide employed from the accepted value, the optical density changes as follows: for 0.05 mg Sb by 9%, for 0.2 mg of Sb by 5%, and for 0.5 mg of Sb by 2%.

By working at high iodide concentrations and consequently at high thiourea concentrations, it is possible to increase the sensitivity 2 – 3 times, but even under the given conditions, it is possible to determine 0.002% Sb in aliquots of 0.5 g. The sensitivity is increased 10 times if the complex is measured colorimetrically in a diethyl ether medium or in a medium of another extracting solvent [4].

In increasing the thiourea concentration from 0.1 to 1 g in 50 ml, the optical density remains unchanged, but the stability of the complex with time decreases; in the presence of 0.1 – 0.2 g thiourea, the optical density is constant for 15 – 24 hours, but when 0.5 – 1 g of thiourea is present, the color beings to weaken after only 3 hours, and after 5 – 6 hours, turbidity as a result of sulfur separation appears – the sulfur is an oxidation product of thiourea.

When more than 20 mg of copper or iron is present, it is necessary to increase the thiourea content 2 – 3 times.

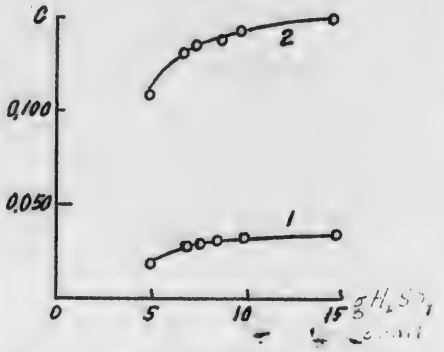

Fig. 1. The relation between optical density of solutions and the concentration of sulfuric acid: 1 - 0.05 mg in 50 ml; 2 - 0.2 mg in 50 ml.

Fig. 3 shows that the color of the complex follows Beer's law only in a narrow range of optical densities, predominantly at low antimony concentrations when the concentration of excess iodide is practically constant. The molar extinction coefficient (with a blue filter) is 1620 for a content of 0.02 mg; 1318 for 0.2 mg, and 533 for 2.0 mg of antimony in 50 ml of solution.

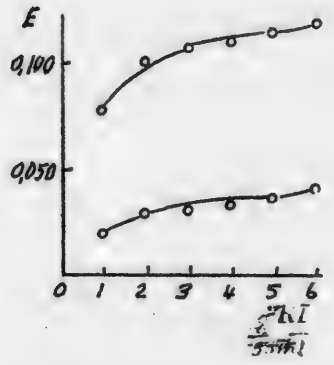

Fig. 2. Relation between optical density of the solutions and potassium iodide concentration: lower curve - 0.05 mg in 50 ml; upper curve - 0.2 mg in 50 ml.

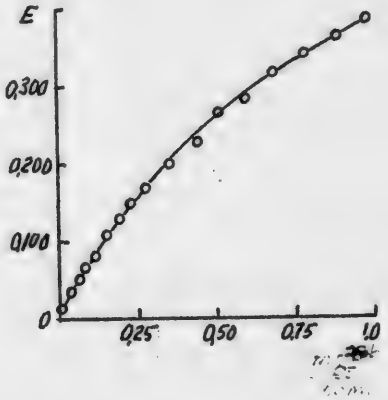

Fig. 3. Calibration curve. 30 mm cuvette, blue filter (400 – 450 mμ).

In order to decompose the ore and simultaneously remove antimony from interfering elements, it is expedient to use a method of sulfurization based on fusion with a mixture of sodium carbonate and sulfur [5, 6]. Thio- salts of antimony, arsenic, and tin, and also the thio- salts of any copper and mercury which may be present. Iron as a sol may also pass through the filter. All these interfering elements are masked by thiourea.

Bismuth is retained on the filter as a precipitate, whatever its relative amount with respect to antimony.

The polysulfides are broken down and the test solution made ready for colorimetric determination by treating the filtrate with a mixture of sulfuric and nitric acids with hydrogen peroxide, and subsequent evaporation of the solution until most of the sulfuric acid has been removed. By dissolving the salt residue in the presence of sulfuric acid, the danger of losing antimony by hydrolysis is removed. This can be carried out for contents of up to 6 mg of antimony in the test.

It is of interest to note a fact which we observed several times; viz., that for antimony contents no greater than 0.5 mg, the weakly acid salt residue can be dissolved in hot water alone and filtered without loss. Our experiments showed that an appreciable sodium sulfate concentration favors the stability of antimony sulfate to hydrolysis in the given case. The presence of iron and ammonium sulfates, on the other hand, favors hydrolysis.

The method was checked on ores, synthetic mixtures, and standard metal and alloy samples (tablets). The latter were dissolved in acids; antimony was precipitated with ammonia, using ferric hydroxide as a collector and was then subsequently determined as described below.

The relative experimental error for a content of up to 0.1% antimony varies within the limits 3 – 10%; for higher antimony concentrations, the error does not exceed 5%.

Maximum light absorption by the iodide-antimony complex occurs in the ultraviolet; for small amounts of antimony, therefore, a violet light filter is best (410 m_μ).

REAGENTS USED

1. Sintering mixture. Finely ground anhydrous sodium carbonate and stick sulfur, mixed in the ratio 4:3.

2. Sulfuric acid (1.42) (470 g/liter).

3. Solution for polysulfide oxidation. Two volumes of sulfuric acid (1.42) (470 g/liter) are mixed with one volume of hydrogen peroxide. The mixture is kept in a cool, dark place.

4. Sulfuric acid, 1.84.

5. Nitric acid, 1.4.

6. Potassium iodide-thiourea solution. 10 g thiourea and 150 g potassium iodide are dissolved in water in a 1-liter standard flask and made up to the mark. The solution keeps for 2 weeks.

7. Sodium sulfate, 1% freshly prepared solution.

8. Standard antimony solutions: 0.5 g and 0.1 g of antimony are dissolved with heating in 20 ml of 1.84 sulfuric acid. The cooled solutions are transferred to 1-liter standard flasks, and 1.42 sulfuric acid added to bring the volume up to the mark.

The two solutions thus prepared contain 0.5 mg/ml of antimony (A), and 0.1 mg/ml of antimony (B). By diluting solution B five times with 1.42 sulfuric acid, solution (C) with a concentration of 0.02 mg/ml antimony is prepared.

ANALYTICAL PROCEDURE

0.1 – 0.5 g of finely ground ore is mixed in a No. 2 porcelain crucible with 6 times its weight of sintering mixture and the charge covered with another 0.3 g of the same mixture. The crucible plus lid is placed either in a cold

muffle or one not hotter than 150° and gradually heated up to 300°; this temperature is maintained for 20 minutes. At this stage formation of polysulfides occurs and the excess sulfur burns. The temperature is then increased to 400-450° and kept here again for 20 – 30 minutes. During this second stage, the oxide and sulfide compounds of antimony are converted into sulfo salts. Higher temperatures must not be used; otherwise partial decomposition of the sulfo salts occurs.

The crucible is cooled and placed in a 100 ml beaker, 15 ml of water is added, and the whole taken up to the boil. The sintered mass is detached from the crucible and leached out. The glaze of the porcelain should be undamaged. The crucible is washed, and the washings filtered into another 100 ml beaker. The precipitate on the filter is washed 2 – 3 times with sodium sulfite solution. The precipitate containing the sulfides of Group 3 and 4 cations and the silica residue can be used for the determination of bismuth. The filtrate is usually colored golden-yellow or yellowish-brown, but it is sometimes greenish as the result of the presence of small amounts of iron sulfide; this, however, does not interfere with antimony determination.

Six to eight ml of the solution for oxidation of polysulfides is added. When this is done, sulfur should be precipitated as well as Group 5 sulfides. The solution is evaporated to a volume of 5 – 8 ml, 3 ml of nitric acid is added, and then evaporation is continued until white fumes of SO_3 appear. In the presence of nitric acid, the sulfur collects together into a lump which it is easy to filter. The inside of the beaker is washed down, and evaporation continued until the sulfur trioxide fumes begin to thin out, after which the beaker is removed from the heating source. If the amount of antimony is high (>1%), a point which it is easy to check on from the orange color of the precipitate after decomposition of the sulfo-salts, then evaporation is stopped at the stage when copious SO_3 fumes are being given off, and the salt residue forms a syrupy liquid (on cooling). The same procedure should be adopted when there is a considerable amount of tin in the ore. To the salt mixture obtained 5 ml of 1.42 sulfuric acid is added, and the mixture heated until complete solution is effected when 15 ml of hot water is added; the solution is mixed and filtered through a d = 5 cm filter into a 50 ml standard flask. Beaker and filter are washed with a small amount of water, another 5 ml of 1.42 sulfuric acid is added, and exactly 10 ml of the thiourea-potassium iodide solution, and the whole made up to the mark with water.

Color develops in one minute. The color is measured the same day; the blank which is used is carried through all the analytical stages.

If an FEK-M apparatus is used, one should take an SS-8 filter and a 30 mm long cuvette for amounts of antimony between 0.01 – 1 mg, and a 10 mm long cuvette for amounts of antimony between 1 – 6 mg.

Calibration curves (tables) are built up by means of standard solutions of antimony and reagents. The total volume of standard solution and sulfuric acid 1.42 should amount to 10 ml; tenths of a milliliter need not be taken into account. The blank should be one made up from reagents only. Visual colorimetric determination can also be carried out; this is best done by means of a standard scale in flat bottomed, 35 mm diameter cylinders. Color intensity is measured along the vertical axis of the cylinder against a white background.

The method described is applicable to ores of varying composition containing up to 3% of antimony, on an aliquot of 0.1 g. Forty to fifty analyses could be carried out in 2 days by one analyst.

TABLE

Results of Antimony Determinations in Synthetic Mixtures and Standard Samples

Amount of Sb taken in mg	Amount of Sb found in mg
0.05	0.045; 0.050; 0.050
0.20	0.20; 0.19; 0.19
2.0	1.99; 1.99; 1.96
0.20 + 10 mg Cu + 10 mg Sn + 10 mg As	0.20; 0.19
0.05 + 0.5 mg Hg + 5 mg Fe	0.05; 0.045
0.5 g ore	0.085
" " " + 0.1 mg Sb	0.18; 0.18
" " " + 0.1 mg Sb + 1 mg Bi	0.18; 0.18
2 mg Bi without antimony	0.00
" " " + 0.2 mg Sb	0.20; 0.19; 0.20
" " " + 0.05 mg Sb	0.045; 0.045; 0.050
0.2 g sample of ore	0.25; 0.24
" " " " " + 40 mg Cu + 20 mg Fe + 10 mg Bi	0.24; 0.23; 0.24
S.O. 91 nickel (~0.01% Sb)	0.014; 0.014%
S.O. 143 brass (<0.002% Sb)	0.001; 0.001%
S.O. 89 bronze (0.25% Sb)	0.25; 0.25; 0.27; 0.25%

SUMMARY

1. The use of thiourea as a reducing agent and complexing agent makes the colorimetric determination of antimony by means of the iodide-antimony complex method more accurate and selective. Using this method it is possible to determine antimony in the presence of copper, iron, tin, arsenic, and mercury.

2. The effect of reagent concentrations, other elements, and other factors on the optical density of the solutions has been studied. Optimal conditions for the photocolorimetric determination of antimony have been established.

3. By sintering the test sample with sodium carbonate and sulfur at 400 – 450°, followed by decomposition of the sulfo salts formed, the antimony can be separated from interfering elements and its determination in a large number of ore samples of varying composition speeded up.

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A NEW MICRO METHOD FOR THE DETERMINATION OF ANTIMONY AND ITS QUANTITATIVE SEPARATION AS STIBINE

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One of the properties which arsenic and antimony have in common is the capacity of their compounds to be reduced in acid media by nascent hydrogen to arsine and stibine respectively.

It is known, however, [1,2] that while trivalent arsenic in acid media is quantitatively reduced to arsine, no success has hitherto been recorded of the quantitative reduction of antimony to stibine. The difficulty of reducing antimony can be explained by the instability of stibine, which is easily oxidized to elemental antimony, which is then lost to determination. In addition, antimony (III) is more easily precipitated than arsenic (III) on the more electro-negative metals (zinc, iron, aluminum, cadmium, etc.), and thus when these react with acid, antimony does not participate in the reduction reaction to give stibine.

As a result the reduction of antimony (III) to stibine requires special conditions which do not include the reaction indicated above. In the literature [3] it is usually pointed out that micro amounts of antimony (III) are reduced to stibine under the same conditions as for conversion of arsenic to arsine.

Sanger and others [5,6] recommend that micro amounts of antimony (III) be reduced by nascent hydrogen obtained by the interaction of hydrochloric acid and zinc or by electrolysis with a lead cathode over which a stream of hydrogen is passed. In this last method, reduction of antimony (III) to stibine must be carried out in a large excess of hydrogen introduced from outside. We have been unable to find results re the quantitative reduction of antimony (III) to stibine.

In most investigations it is almost invariably necessary to combine quantitative determination with qualitative reactions (e.g., determination of micro amounts of antimony in biological material); it is most convenient to carry out the reactions for antimony after its reduction to stibine.[1)] Stibine obtained as the result of the reduction reaction is very reactive and enters into many volumetric and oxidation-reduction reactions (with elemental iodine, silver nitrate and mercuric chloride or bromide, etc.). These reactions are also used for the determination of antimony after its reduction to stibine.

In the present paper we have described a new iodo-thiourea method for the determination of antimony, the conditions for carrying out the method, and the extent of the reduction of micro amounts of antimony (up to 5 mg) with nascent hydrogen:

$$SbO_2^- + 3Zn + 7H^+ \rightarrow H_3Sb + 3Zn^{2+} + 2H_2O.$$

---

1) E. B. Sandel points out [4] that the method of determining micro amounts of antimony (III) after reduction to stibine has not been worked out fully enough.

Methods for determining antimony have usually a colorimetric finish based on the formation of a yellow color on paper soaked with mercuric chloride or bromide. These methods are difficult to carry out and give low results because small amounts of stibine do not give colors with paper soaked in the mercuric salts mentioned [7]. This is a drawback of Sanger's colorimetric method.

The stibine formed reacts in a glass tube with elemental iodine to give a non-volatile orange yellow antimony tri-iodide:

$$H_3Sb + 3I_2 \rightarrow SbI_3 + 3HI$$

which collects as one or two rings on the tube walls. This can be used as a qualitative reaction for antimony ions.

The antimony tri-iodide in the presence of potassium iodide is washed into a tartaric acid solution. In this solution iodine is reduced with ascorbic acid, while the antimony is easily converted into antimonyl tartrate by heating the solution.

Determination of antimony (III) in the solution obtained is based on the capacity of organic bases to give difficultly soluble colored double iodides $[R \cdot H]SbI_4$ (R – organic base). This reaction is used for the colorimetric determination of antimony. Thiourea was chosen instead of pyridine, the base described in the literature [3]; the advantage of thiourea as compared with pyridine is the greater stability of the thiourea iodide complex with antimony.

EXPERIMENTAL

Colorimetric Determination of Antimony by the Iodide-Thiourea Method

Before applying the iodide-thiourea method, it was essential to get accurate and reproducible results for antimony determinations in solutions of known antimony concentrations.

Determinations were carried out as follows: 0.5 ml of 20% potassium iodide solution containing 0.1% ascorbic acid was introduced into a 30 ml test tube and 0.5 ml of 8% thiourea and 10-15 ml of 8 N sulfuric acid added; finally 1-5 ml of antimony test solution was added. After thorough mixing, the color obtained was compared with a standard color prepared in the same way but for which a standard antimony solution was measured out accurately from a micro-buret, until the colors in the tubes matched. The final volumes were levelled with 8 N sulfuric acid (colorimetric titration method).

There was no need to use gelatin or gum arabic as protective colloids.

As a preliminary, we studied the stability at ordinary temperatures of the iodide-antimony complexes formed with various organic bases: pyridine, β-picoline, urotropine, urea, and thiourea. Two drops of starch solution were added to the test solution for control. Darkening of the solution in the course of a definite time interval (minutes, hours, days) indicated decomposition of the complexes.

The results obtained are given in Table 1.

These results show that the iodide antimony complexes formed with pyridine, β-picoline, urotropine and urea were only stable 10-20 minutes; the stability of these complexes with thiourea is better; these complexes do not break down within 24 hours.

In order to check on the methods which we have put forward, several determinations of antimony were made in solutions of known concentration. The results of these experiments are given in Table 2.

These results indicate that antimony can be determined fairly accurately and with good reproducibility.

In determining antimony with thiourea, the following conditions must be observed: a) equal volumes of thiourea and potassium iodide must be added to both standard solutions and the solutions to be determined colorimetrically. A proportional decrease in the stipulated amounts of reagents used in the standard and test solutions is permissible for very small concentrations of antimony in the test solution. Thiourea, in amounts greater than that indicated, weakens the color slightly, while smaller amounts of thiourea than that stipulated lead to instability of the color.

TABLE 1

Stability of Iodide-Antimony Complexes
Formed with Organic Bases

Base	Stability									
	10 min.	20 min.	30 min.	40 min.	60 min.	1.5 hrs.	2 hrs.	6 hrs.	12 hrs.	24 hrs.
Pyridine	+ −	−	−	−	−	−	−	−	−	−
β-Picoline	+ −	−	−	−	−	−	−	−	−	−
Urotropine	+	+ −	−	−	−	−	−	−	−	−
Urea	+ −	−	−	−	−	−	−	−	−	−
Thiourea	+	+	+	+	+	+	+	+	+	+ −

Notes. (+) is the time in the course of which the complex is stable; (+ −) is the time at the end of which the complex decomposes; (−) after the expiration of this time, the complex is broken down.

TABLE 2

Results of Antimony Determinations
by the Iodide-Thiourea Method

Amount of antimony taken, in mg	Antimony found, in mg	% Antimony found
0.002	0.002; 0.002	100.0
0.003	0.003; 0.003	100.0
0.005	0.005; 0.005	100.0
0.008	0.008; 0.008	100.0
0.010	0.010; 0.009; 0.010	97.0
0.050	0.048; 0.050; 0.050	98.6
0.100	0.102; 0.100; 0.100	100.7
0.250	0.247; 0.249; 0.250	99.0
0.500	0.502; 0.504; 0.495	100.0
1.000	1.000; 0.990; 0.992	99.4
3.000	3.006; 2.990; 2.990	99.8
5.000	5.020; 5.010; 5.000	100.2

b) The optimal acidity of the test and standard solutions when made up to the final volume should be equal to or greater than 6 N.

c) Oxidizing agents should be absent (nitrogen oxides, etc.); antimony used for determination should be either tri- or quinquevalent; quinquevalent antimony in the presence of HI is reduced to the tri form; mercury, bismuth, lead, copper, iron and excessive amounts of arsenic and tin should be absent.

d) The absolute amount of antimony in the aliquot to be determined should not exceed 200 − 250 μg and should not be less than 2 μg.

Liberating and Fixing the Stibine

The extent of the reduction of antimony (III) to stibine was studied when the hydrogen evolved was produced by the following reactions:

1) 4 M sulfuric acid and zinc;
2) 4 M sulfuric acid and aluminum;
3) 4 M sulfuric acid and "coppered" zinc.
4) 4 M sulfuric acid plus "coppered" zinc plus stannous chloride.
5) 4 M sulfuric acid, zinc, and potassium bromide.
6) concentrated hydrochloric acid (37%) and zinc.
7) concentrated hydrochloric acid (37%) and amalgamated zinc.

Tests were made as follows.

Apparatus for liberating and fixing H_3Sb

The test solution of antimony (III), 15 ml of acid and 6-8 g zinc [or as the case may be, 2-3 g aluminum, 2 ml of 20% potassium bromide, and 1 ml 20% stannous chloride (II)] were placed in a 30 ml test tube (see diagram). The test tube was fitted with a ground glass test tube to which was sealed a tube which served as a receiver for the stibine. This receiver should be 0.6-0.8 cm diameter and 10-12 cm long. Inside this tube was fixed 0.5-0.6 g of cotton or glass wool strewn with ca. 80 mg of iodine crystals. The wool was given a preliminary wash with water and dried. The joint should preferably be a ground glass one, though a rubber bung may be used as a last resort. The stibine evolved passed into the receiver, where it was absorbed by the elemental iodine.

If any stibine is evolved, it reacts with the elemental iodine to give characteristic orange yellow color rings on the tube walls. Even as little as 2 μg of antimony, on reduction to stibine with concentrated hydrochloric acid and amalgamated zinc, gave an orange red ring of antimony iodide on tube walls of 0.4 cm diameter, while amounts of ca. 1 mg and more of antimony gave 2 – 3 rings.

From the number and size of orange yellow rings formed only in the lower parts of the receiving tube, the analyst can get an approximate idea of how much antimony has taken part in the reaction. This is an important point since it will be necessary in the later stages to know how much liquid to use for direct colorimetric determination of the antimony, and this will depend on the amount of antimony present.

Apart from visual observation (fixation of stibine in the lower part of the tube), the analyst can carry out reactions which indicate the quantitative absorption of H_3Sb by elemental iodine (reactions of Guzeit and others).

When the reaction between zinc and acid was complete, usually after 30-40 minutes, the reaction between amalgamated zinc and concentrated hydrochloric acid took at least 2 hours, the receiving tube was disconnected from the test tube; 0.25 ml of 20% potassium iodide was then introduced into the tube from above and the tube subsequently washed out a few times with hot water, also through the top. The wash liquor was collected in a 35-40 ml beaker containing 2-3 ml of 20% tartaric acid. During this operation about 8-10 ml of liquid was collected which should contain all the antimony which has been reduced to stibine and absorbed by elemental iodine. This liquid also contained the excess iodine which was removed by the careful addition of ascorbic acid dropwise; 1-2 drops of 0,1% ascorbic acid solution was finally added in excess. The final solution obtained was boiled for 2-3 minutes. When the amount of antimony was small, it was boiled until the volume was only 3-4 ml. When a yellow color appeared during boiling, 1-2 drops of 0.1% ascorbic acid solution was added. The solution was transferred quantitatively from the beaker to a 25-100 ml standard flask, cooled, and made up to the mark with 20% tartaric acid. When a fairly large amount of antimony was present, aliquots of 1-2 ml were taken from this solution for colorimetric determination. When the amounts of antimony were small, the whole original solution of 3-4 ml (i.e., solution before being made up to standard volume) was used for the determination. Results on the determination of antimony after reduction to H_3Sb with hydrogen formed by the interaction of H_2SO_4 and Zn are given in Table 3.

These results show that antimony can be determined after reduction in amounts equal to 25.0 – 56.0%. The remainder of the antimony is precipitated on the zinc, or on reduction is transformed into the elemental state. Amounts of antimony less than 15 μg were not determined by this method of reduction.

TABLE 3

Determination of Antimony after Reduction to H_3Sb with Hydrogen Evolved by Interaction of H_2SO_4 and Zn

Antimony taken, in mg	Antimony found, in mg	Difference	Antimony found, in %
3.000	0.920	2.080	30.7
2.000	0.730	1.270	36.5
1.500	0.608	0.892	40.5
1.000	0.250	0.750	25.0
0.800	0.410	0.390	51.2
0.500	0.280	0.220	56.0
0.250	0.140	0.110	56.0
0.100	0.051	0.049	51.0
0.050	0.022	0.028	44.0
0.020	0.009	0.011	45.0

In the next series of experiments, we substituted aluminum for zinc. On heating, aluminum reacted with sulfuric acid, but no stibine was evolved. Antimony in the form of a dull black, velvety layer precipitated on the aluminum. The following mixture was then tried for reducing antimony (III) to H_3Sb: sulfuric acid plus "coppered" zinc (i.e., zinc, covered with copper as a result of the reaction $Zn + CuSO_4$). Under these conditions H_3Sb was evolved in insignificant amounts. Antimony precipitated on the copper and zinc. A similar phenomenon was observed when sulfuric acid plus "coppered" zinc and stannous chloride (II) was used. Metallic zinc reduced the Sn^{2+} and $[SnCl_6]^{2-}$ ions to the metal. The latter separated out as a spongy bulky precipitate.

$$Sn^{2} + Zn \rightleftarrows Zn^{2+} + Sn;$$

$$[SnCl_6]^{2-} + 2Zn \rightleftarrows 2Zn^{2+} + Sn + 6Cl^{-}.$$

The hydrogen evolved by the reaction of zinc and acid can also be used up to reduce Sn^{2+} and $[SnCl_6]^{2-}$. Our experiments showed that practically no stibine is evolved in the system acid – zinc – stannous chloride (II).

In all these experiments not more than 10% of the antimony introduced could be determined by reduction to stibine. It became essential, therefore, to find other suitable conditions whereby antimony (III) could be quantitatively reduced to stibine. The evolution of H_3Sb by the reaction of sulfuric acid and zinc in the presence of potassium bromide and also of hydrochloric acid and zinc was studied. Under these conditions 50 to 90% of antimony (III) was reduced to stibine.

The conditions under which stibine was formed were accordingly changed again in further experiments. By reduction with nascent hydrogen, antimony (III) can be partially precipitated on metals which are in front of it in the EMF series. In order to prevent precipitation and also to slow down the reaction between metal and acid, amalgamated zinc was tried. The amalgamated zinc reacted slowly with acid, but the hydrogen on the mercury surface had a high over-voltage. Such hydrogen, it was proved, quantitatively reduced the antimony (III) to stibine. Only a small amount of hydrogen thus prepared was necessary for this quantitative reduction to stibine. Results for the determination of various amounts of antimony are given in Tables 4 and 5.

As we see from the data of Table 4, antimony can be quantitatively determined (with accuracy of $\pm$ 0.3%) after reduction to H_3Sb with hydrogen obtained by the interaction of hydrochloric acid and amalgamated zinc.

These results show the reproducibility of the method.

We established further that half of the hydrochloric acid can be substituted by 4 M sulfuric acid without affecting the results.

TABLE 4

Determination of Antimony (from 2 to 100 μg) after Reduction to H_3Sb with Hydrogen, Obtained by the Interaction of Hydrochloric Acid and Amalgamated Zinc

Antimony taken, in μg	Antimony found, in μg	Difference, in μg	Antimony found, in %
2.0	2.0; 1.9; 1.9	0.1	96.5
3.0	3.0; 2.8; 2.9	0.1	97.0
5.0	4.9; 4.9	0.1	98.0
8.0	7.8; 8.0	0.1	98.7
10.0	9.7	0.3	97.0
12.0	11.7	0.3	97.5
15.0	14.8	0.2	98.0
20.0	20.1	0.1	100.5
25.0	24.2	0.8	96.80
30.0	29.0	1.0	97.0
40.0	39.1	0.9	97.9
50.0	49.2	0.8	98.4
80.0	81.0	1.0	101.2
100.0	97.8	2.2	97.8

TABLE 5

Determination of Antimony (from 100 μg to 5 mg) after Reduction to H_3Sb with Hydrogen, Obtained by the Interaction of Hydrochloric Acid and Amalgamated Zinc

Antimony taken, in mg	Antimony found, in mg	Difference, in mg	Antimony found, in %
0.100	0.097	0.003	97.0
0.200	0.197	0.003	98.3
0.400	0.392	0.008	98.0
0.500	0.488	0.012	97.6
0.800	0.788	0.022	98.5
1.000	0.978	0.022	97.8
2.000	2.010	0.010	100.5
3.000	2.980	0.020	99.3
4.000	4.030	0.030	100.7
5.000	5.000	0.000	100.0

Conditions for the Quantitative Reduction of Antimony (III) to Stibine during the Reaction of Amalgamated Zinc with Hydrochloric Acid

a) Antimony is more easily reduced to stibine and also to elemental antimony than arsenic; e.g., when the reduction reaction is very vigorous, some of the antimony is converted into the elmental stage and is, therefore, not available for conversion to stibine. Consequently, hydrogen evolution by the action of hydrochloric acid and amalgamated zinc should not be too vigorous. The reaction should proceed slowly and smoothly without any sudden surges and frothing. The volume of liquid should not increase appreciably as the result of hydrogen evolution. If the amalgamated zinc is properly prepared, this condition will be observed.

b) The hydrochloric acid used for reacting with amalgamated zinc should be at least 9 M (ca. 30%).

c) Reduction of antimony (III) to stibine should be effected at 15 to 20°; the apparatus is immersed in cold water if overheating occurs.

d) Reduction of antimony (III) to stibine should take not less than 2 hours.

e) During the reduction to stibine, reducing agents (HI, HBr) and also copper, tin, aluminum, or their ions should be absent.

I should like to thank I. P. Alimarin for his help in writing this article.

SUMMARY

1. A new method for the colorimetric determination of antimony (III) with thiourea is proposed. The advantages of this method as compared with the pyridine-iodide method is the stability of the iodide-antimony complex over a period of 24 hours.

2. Optimal conditions are given for the quantitative reduction of antimony (III) to stibine by the reaction of amalgamated zinc with concentrated hydrochloric acid. Results with good reproducibility are obtained with an error of ± 3.0%.

3. The stibine evolved by the procedure outlined is quantitatively absorbed in a receiving tube containing elemental iodine, and the antimony is subsequently converted into antimonyl tartrate.

4. In the course of the quantitative determination of antimony, a reaction is employed by means of which antimony can be detected qualitatively by the formation of orange yellow antimony iodide. The reaction is specific; its limiting sensitivity is 2 μg antimony.

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DETERMINATION OF ACRYLONITRILE BY A CYANO-ETHYLATION REACTION

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Acrylonitrile $CH_2=CH-CN$ is produced and used on a large scale for the preparation of synthetic rubber and plastics, so that methods for its analysis are of practical importance. Since the qualitative composition of mixtures containing it may be rather varied, it is necessary to have various methods of determining acrylonitrile which are suitable for the various conditions under which it is found.

The physical methods which have been suggested for its determination – spectrophotometric [1], polarographic [2], and spectroscopic (infra-red) [3] – are not generally applicable; moreover they require special apparatus. Other methods which are simple by virtue of the use of a titration technique cannot be used for determination of acrylonitrile in colored solutions, because the end point itself is determined by a color change. One of these methods is based on the oxidation of the double bond in acrylonitrile with permanganate solution in the presence of sulfuric and hydriodic acids [4]. The error in this case is $\pm$ 5%.

A second method uses the reaction between acrylonitrile and dodecylmercaptan, the excess of which is titrated with iodine. The accuracy of this method is $\pm$0.22% [5]. It has been shown recently [6] that the simple volumetric titration of dodecylmercaptan with iodine can be replaced by potentiometric titration so that acrylonitrile can be determined in colored solutions.

The usual method of analyzing nitriles – alkaline saponification – in particular in the presence of hydrogen peroxide [7], and subsequent determination of the ammonia evolved, is not accurate enough in the case of acrylonitrile, and is not always practicable, since the nitrile groups of other compounds which accompany technical acrylonitrile are hydrolyzed under the same conditions (ethylenecyanohydrin, acrylonitrile polymers, etc.).

Research on the cyano-ethylation of α-amino acid derivatives [8] led us to develop a fairly simple method for the quantitative determination of acrylonitrile. α-Amino acids in the form of their alkali salts react easily with acrylonitrile in aqueous solution [9]:

$$NaOOCCHNH_2 + CH_2=CHCN \rightarrow NaOOCCHNHCH_2CH_2CN.$$
$$\quad\;\; R \qquad\qquad\qquad\qquad\quad R$$

The new method proposed is based on a reaction which proceeds quantitatively between acrylonitrile and an aqueous solution of the potassium or sodium salt of glycine, the most readily available amino acid. To the aliquot of acrylonitrile a known amount of a solution of glycine of known concentration is added; on completion of the reaction, excess of the latter is determined gasometrically by Van Slyke's method, by means of which only amino acids containing the primary amino group are determined. This method is applicable in the case of colored solutions, and permits determination of acrylonitrile with an accuracy of $\pm$ 1% in mixtures containing ethylenecyanohydrin, water, and acrylonitrile polymers.

Van Slyke determinations are carried out in the usual apparatus [10]. We used a new micro apparatus which was made in the Protein Chemistry Laboratory of Moscow University by Ioanisiani [11]. The main feature of this apparatus is the use of an ordinary medicinal glass syringe as a reaction vessel of variable

volume, which simplifies, speeds up, and makes the determinations more accurate.

Conditions were chosen such that on the one hand possible side reactions, such as the saponification of acrylonitrile and dicyano-ethylation:

$$NaOOCCHNH_2 + CH_2=CHCN \rightarrow NaOOCCHN(CH_2CH_2CN)_2,$$
$$\quad R \qquad\qquad\qquad\qquad\qquad\qquad\quad R$$

are excluded, while on the other hand, the reaction between glycine and acrylonitrile is quantitative. The conditions for analytical determination of acrylonitrile finally chosen were as follows: the amount of acrylonitrile in the aliquot to be analyzed should be ca. 0.1 g, while the molecular ratio of reagents should be glycine:acrylonitrile 2.5:1; solvent – water – 10 ml; reaction time, 1 hour; temperature – room. Attempts to lower the reagents ratio and to increase the total concentration in solution, and also cutting down reaction time by heating, all led to low results. Thus, on using the conditions given above but cutting down the time to 30 minutes, only 84.5% of the acrylonitrile reacted. Lower alcohols which complicate carrying out Van Slyke's gasometric determination of amino groups, interfere with acrylonitrile determination. Other compounds which can interfere are those which contain an active double bond of the acrylonitrile type (crotonitrile, acrylates) because they also react with glycine, as shown by preliminary experiments.

Results are given in the table for the analysis of pure acrylonitrile samples and of acrylonitrile in admixture with water and ethylenecyanohydrin:

Expt. No.	Aliquot taken in g	Composition of sample			Acrylonitrile found in %
		Acrylonitrile	Water	Ethylenecyanohydrin	
1	0.1047	100	–	–	99.8
2	0.1075	100	–	–	100.1
3	0.1127	100	–	–	100.2
4	0.1094	100	–	–	101.0
5	0.1123	96.7	–	3.3	96.8
	0.1009				96.9
6	0.1120	92.7	2.1	5.2	93.4
7	0.1075	91.1	1.4	7.5	91.6
	0.1273				92.3
8	0.2354	49.2	10.9	39.9	49.1
	0.2010				49.7
9	1.0432	10.1	30.2	59.7	9.5
	1.1102				9.9

EXPERIMENTAL

Reagents

1. Glycine solution. 38 g (ca. 0.5 M) of glycine is dissolved in water and 28 g (ca. 0.5 M) of potassium hydroxide and 1 g of sodium fluoride (for prevention of mold formation) added, and the whole diluted to 1 liter. The solution can be kept for a long time.

2. 30% solution of sodium nitrite.

3. Permanganate solution (50 g of potassium permanganate and 25 g of sodium hydroxide in 1 liter of water).

4. 50% potassium iodide.

5. 30% sodium hydroxide.

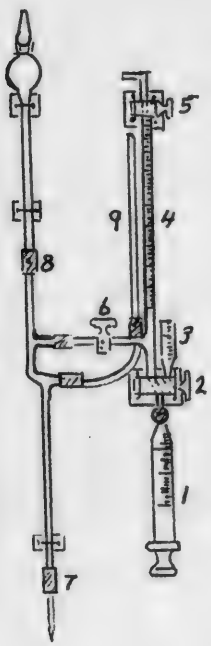
6. Glacial acetic acid.

7. Acrylonitrile dried over calcium chloride and twice distilled, boiling point 77 – 78° (760 mm) was used for standardizing the glycine solution.

Analytical Procedure and Apparatus

10 ml of the glycine solution is pipetted into a 50 ml conical flask fitted with ground glass stopper, and an aliquot of test material added (the amount of acrylonitrile in the aliquot should be ca. 0.1 g). The flask is shaken gently and allowed to stand stoppered for 1 hour at room temperature, after which it is neutralized with acetic acid (8-10 drops of glacial acetic acid) to a phenolphthalein end point (the neutralized solution can be kept for an indefinite time).

1 ml of 50% potassium iodide is next added[1], and the solution is diluted to 100 ml with water in a standard flask. 1 ml of this solution is taken in order to determine amino nitrogen gasometrically in the Ioanisiani apparatus (see diagram).



Amino nitrogen is determined as follows: 1 ml of solution is introduced into funnel 3 by means of a pipet. Having passed it through tap 2 into the syringe, 1, 3 is washed with 1 ml of water, and this is also passed into the syringe. 5 ml of nitrous acid solution (prepared by shaking 1 ml glacial acetic acid with 4 ml 30% $NaNO_2$ solution in a 10 ml measuring cylinder) is next passed through funnel 3 into syringe 1. All these operations are carried out in such a way that when tap 2 is closed, the bore of the tap and also the bottom of funnel 3 are filled with liquid. Ca. 3 ml of 30% NaOH is placed in 3, and the syringe shaken for 3 minutes. When the reaction is complete, the alkali is allowed into the syringe, followed by small amounts of alkaline permanganate (4-5 ml), so that on shaking, the oxides of nitrogen are absorbed. When this is done, the syringe piston is moved upward. When alkaline permanganate is clearly visible around the bubble of gas which remains, 1-2 ml of water is carefully passed through funnel 3, and the nitrogen is carefully expelled through tap 2 into the buret by slight compression of the syringe piston. Having closed taps 2 and 3, tap 6 is opened, and with the aid of beads 7 and 8 the levels of water in tube 9 and buret 4 are equalized. When the gas volume has been measured, taps 2 and 5 are opened, and the mixture expelled by means of the piston. The system is washed with a solution of oxalic acid and twice with water.

Acrylonitrile content is determined by means of the formula:

$$\% \text{ acrylonitrile} = \frac{\text{mol. wt. acrylonitrile} \cdot 100}{S \text{ mol. wt. nitrogen} \cdot 10} (T - a) =$$

$$= \frac{53.06 \cdot 100}{S \cdot 140} (T - a) = \frac{37.9}{S} (T - a),$$

where S – is the weight of test mixture; a – the number of milligrams of nitrogen in the solution as determined gasometrically.

$T = \frac{T'}{10}$ (where T' is the number of milligrams of nitrogen in 1 ml of the glycine salt solution) is the standard titer; this is determined in a separate experiment in which pure acrylonitrile, assumed to be 100%, is used instead of the test mixture. T is given by the formula:

$$T = \frac{S_1}{0\ 379} + a_1,$$

1) KI is added in order to get constant results for the determination of glycine.

where S_1 . is the weight of pure acrylonitrile taken; a_1 – the number of milligrams of nitrogen in 1 ml of solution as determined gasometrically.

SUMMARY

A new method has been developed for the analysis of acrylonitrile, which is based on the reaction between the latter and glycine.

By means of this method, acrylonitrile can be determined in colored mixtures which contain water and ethylenecyanohydrin with an accuracy of up to ± 1%.

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ANALYSIS OF SILICO-ORGANIC COMPOUNDS

QUALITATIVE ANALYSIS OF MIXTURES OF ALKOXYSILANES WITH ALCOHOLS AND SILICON TETRACHLORIDE

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Despite the ever increasing use in industry of silico-organic compounds, their analysis has not been developed fully enough. The first qualitative reactions for silico-organic compounds were proposed by Soviet scientists [1-6].

The necessity of analytical methods and production control for silico-organic compounds is obvious, since during the production of these compounds, mixtures with other compounds are inevitably obtained, and the required compounds are only separated from these others in a more or less pure form by a series of operations.

In the present paper we describe a number of methods which we have worked out for the qualitative analysis of mixtures of certain alkoxysilanes with alcohols and silicon tetrafluoride, which are the compounds most often met with in practice

All the compounds which we used for making up synthetic mixtures were subjected to careful purification, and had the requisite physical constants. The inorganic reagents used were chemically pure or analytical grade.

Detection of $SiCl_4$ in Tetramethoxy- and Tetraethoxy Silanes

1. Reaction with Hydrogen Iodide or Potassium Iodide. We found that on heating hydrogen iodide with mixtures of ortho silicic acid esters and $SiCl_4$, free iodine is evolved. Pure $SiCl_4$ reacts in the same way even in the cold.

A mixture of 1-2 ml of test material and 2-3 drops of concentrated hydrogen iodide is heated in a test tube in a glycerol bath, the test tube being first of all covered with ashless filter paper soaked with saturated $Hg(NO_3)_2$ solution. Any $SiCl_4$ present will lead to a brown coloration of the paper. If the paper turns red this indicates the presence of the methyl or ethyl esters of ortho silicic acid [4], and the absence of $SiCl_4$.

Iodine is also evolved when $SiCl_4$ vapor reacts with potassium iodide.

The evolution of iodine by the action of $SiCl_4$ on HI or KI can be explained by the oxidizing properties of $SiCl_4$ [7].

$$2SiCl_4 + 2KI \longrightarrow Cl_3Si{-}SiCl_3 + 2KCl + I_2.$$

2. Reaction with Aniline or with an Aniline Solution of Tetramethyldiaminobenzophenone. In order to detect $SiCl_4$ in methoxy and ethoxysilanes, it is also possible to use the reaction with aniline or an aniline solution of tetramethyldiaminobenzophenone [2].

To 5-6 drops of test mixture is added 1-2 drops of aniline or an aniline solution of tetramethyldiaminobenzophenone. If $SiCl_4$ is present, then in the first instance a white precipitate appears, while in the second instance, a yellow precipitate is formed which is soluble in excess reagent.

3. Reaction with Water. It is also possible to detect $SiCl_4$ in methoxy and ethoxy silanes by the action of water. Hydrochloric acid is formed by the action of water on $SiCl_4$, and this can be detected with an indicator.

4-5 drops of test solution are placed in a small test tube, blue litmus paper is also introduced, and a few drops of water added rapidly. If $SiCl_4$ is present, a white gelatinous precipitate of silicic acid forms, while the litmus paper turns red.

4. Reaction with Potassium Bichromate and Nitric Acid. We found that potassium bichromate in dilute nitric acid gave a characteristic blue-violet color with methoxy and ethoxy silanes. If $SiCl_4$ is present, the rate of formation of this color is slowed down considerably.

To 5 ml of dilute nitric acid (1:2) contained in a test tube is added with cooling 5 drops of 5% potassium bichromate and 1-2 ml of test material, and the whole shaken up.

A blank is made simultaneously. In a test tube containing ester which contains $SiCl_4$, the blue color appears about 2-3 times slower than in esters which do not contain $SiCl_4$.

5. Reaction with Ferric Ferrithiocyanate. We found that the presence of $SiCl_4$ in tetramethoxy and tetraethoxy silanes leads to decolorization of $Fe[Fe(SCN)_6]$ solution.

A small lump of paper treated with an alcoholic solution of $Fe[Fe(SCN)_6]$ and 1-2 ml of CH_3OH is placed in a small test tube. The alcohol will be colored red by the $Fe[Fe(SCN)_6]$. 8-10 drops of test solution is then added; if $SiCl_4$ is present, the red color disappears.

Results of the analysis of mixtures of methoxy and ethoxy silanes with silicon tetrachloride are given in the Table.

Detection of CH_3OH in $(CH_3O)_4Si$ and of C_2H_5OH in $(C_2H_5O)_4Si$

1. Reaction with Metallic Sodium. In order to detect the corresponding alcohols of tetramethoxy and tetraethoxy silanes reaction with metallic sodium was used.

1-2 ml of test mixture was placed in a test tube and a lump of clean sodium, washed in absolute diethyl ether, added.

Any alcohol present in the test esters will lead to turbulent evolution of hydrogen and the formation of the corresponding alkoxides.

The reaction is very sensitive and less than 1% of alcohol can be detected.

2. Reaction with Ferric Ferrithiocyanate. We found that methoxy- and ethoxy silanes, in contrast to the respective alcohols, do not dissolve $Fe[Fe(SCN)_6]$. The reaction with $Fe[Fe(SCN)_6]$ can therefore be used for the detection of the alcohols in alkoxysilanes.

1-2 ml of test mixture and paper treated with an alcoholic solution of $Fe[Fe(SCN)_6]$ and dried, are placed in a test tube. If alcohol is present, the liquid will be colored rose or red. For mixtures of $(CH_3O)_4Si$ + CH_3OH, the limit of identification is 0.65 mg CH_3OH, and the limiting concentration, 1.0%. For mixtures of $(C_2H_5O)_4Si$ + C_2H_5OH the limit of identification is 2 mg C_2H_5OH. Limiting concentration 1%.

3. Reaction with Silicon Tetrachloride. Reaction with $SiCl_4$ can also be used for the detection of methyl alcohol in methoxy silane.

1-2 ml of test material is placed in a test tube and a piece of blue litmus paper introduced. A few drops of absolutely dry $SiCl_4$ are added. The test tube is stoppered and shaken. If CH_3OH is present the litmus will turn red. Limits of identification, 6.5 mg. The limiting concentration is 5%. In order

TABLE

Result of the Analysis of Mixtures of Tetramethoxysilane and Tetraethoxysilane with Silicon Tetrachloride

Reagent	Indicator	Effect of reaction	Sensitivity, in mg $SiCl_4$	Limiting concentration $SiCl_4$, in %	Temperature °C
		Mixtures of $(CH_3O)_4Si$ + $SiCl_4$			
Hydrogen iodide	$Hg(NO_3)_2$ paper	Brown color	9.7	5	85-95
Potassium iodide	Starch paper + KI	Bluish brown color	6.5	10	70-75
Aniline	–	White precipitate	0.5	1	18-20
Aniline solution of tetramethyldiaminobenzophenone	–	Yellow or orange precipitate	0.5	1	18-20
Water	Blue litmus paper	Change of color of litmus to red + white precipitate	0.16	<1	18-20
Potassium bichromate and nitric acid	(Rate at which blue color appears is slowed down 2-3 times as compared with pure material)			10	18-20
$Fe[Fe(SCN)_6]$	Solution of $Fe[Fe(SCN)_6]$ in methanol	Decolorization of solution	1.3	1	18-20
		Mixtures of $(C_2H_5O)_4Si$ + $SiCl_4$			
Hydrogen iodide	$Hg(NO_3)_2$ paper	Brown color	13	19	110-120
Potassium iodide	Starch paper + KI	Bluish-brown color	6.5	10	70-75
Aniline	–	White precipitate	0.5	1	18-20
Aniline solution of tetramethyldiaminobenzophenone	–	Yellow or orange precipitate	0.65	1	18-20
Water	Blue litmus paper	Litmus paper turns red + white precipitate	0.16 1.2	<1	18-20
Potassium bichromate and nitric acid	(Rate at which blue color appears is slowed down 2-3 times as compared with pure material)			10	18-20
$Fe[Fe(SCN)_6]$	Solution of $Fe[Fe(SCN)_6]$ in methanol	Decolorization of solution	1.3	1	18-20

to detect C_2H_5OH in tetraethoxy silane, heating is necessary.

Detection of the Methyl and Ethyl Esters of Ortho Silicic Acid in the Presence of Alcohols or $SiCl_4$

If only $SiCl_4$ is present, methoxy and ethoxysilanes can be detected by the reaction with borax in the presence of hydrochloric or sulfuric acids [1, 4]. During this reaction methyl borate or ethyl borate are formed which color a burner flame green. Limit of identification for $(CH_3O)_4Si$, 10 mg, while for $(C_2H_5O)_4Si$ it is 20 mg.

If only the alcohols are present, the methoxy or ethoxy silanes can be detected by heating with hydrochloric acid [4]; during this reaction a precipitate of silicic acid is formed which can be colored with methylene blue. Limit of identification, 2 mg of the alkoxysilane.

SUMMARY

1. A scheme for the qualitative analysis of the following mixtures has been worked out: a) tetramethoxy silane and silicon tetrachloride; b) tetramethoxysilane and methyl alcohol; c) tetraethoxy silane and silicon tetrachloride; and d) tetraethoxysilane and ethyl alcohol.

2. Two new qualitative reactions have been found for silicon tetrachloride: a) formation of free iodine on interaction with hydrogen iodide or iodides; b) decolorization of an alcoholic solution of ferric ferrithiocyanate.

3. It has been found that tetramethoxy- and tetraethoxy silanes, in contrast to the corresponding alcohols, do not dissolve ferric ferrithiocyanate. On this basis, a method has been worked out for the qualitative determination of alcohols in alkoxysilanes.

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SPECIFIC ATOMIC GROUPINGS IN REAGENTS FOR TUNGSTATES

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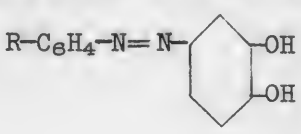
The outstanding research work of L. A. Chugaev [1, 2, 3], who discovered the reaction of α-dioximes with nickel and other ions, is the basis of the theory of specific atomic groupings. This theory has received its furthest development chiefly at the hands of Soviet scientists. In the course of the last 15 years specific atomic groupings have been discovered which determine the analytical reactions of organic compounds with Al^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+}, V^{4+} – Kuznetsov [4,5,6,7,8]; Mg^{2+}, In^{3+} – Kulberg [9,10,11]; and BO_3^{3-} – Korenman [12], etc.

Organic reagents which have been suggested for the detection of tungstates are discussed in the present article, and it is shown that their activity is determined by a definite and specific atomic grouping.

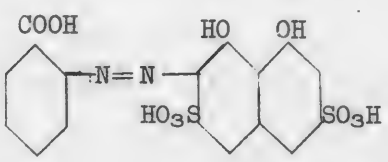
The number of atomic reagents suggested for the detection of tungstates is very limited. Kuznetsov [13], has studied the reactions of a number of azo dyes – pyrocatechol derivatives (I) with tungstates



(I)

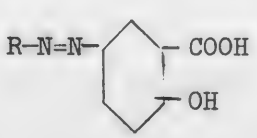
where R = NO_2; SO_3H; NH_2

Kuznetsov [14] suggested a reaction for the detection of WO_4^{2-} involving an azo dye of the composition

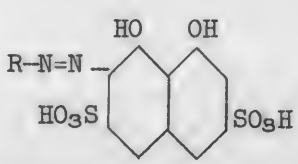


Schäfer [15] used a color reaction with curcumin for detection of WO_4^{2-}. Reactions with uric acid and phenols [16], α-benzoinoxime [17], and others [18, 19] have also been suggested.

During a study of the analytical reactions of azo dyes – salicyl derivatives (II), (19 reagents) and chromotropic acid (III) (10 reagents)



(II)



(III)

where R = C_6H_5; $C_6H_4NO_2$; $C_6H_4SO_3H$; $C_6H_4AsO_3H_2$; $C_6H_4N(CH_3)_2$, etc., we found [20] that under certain conditions of carrying out the reactions, color reactions were given with tungstates despite the considerable variation in reagent composition.

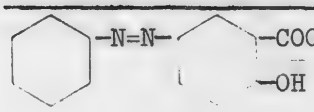
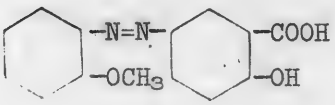
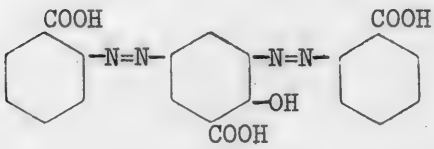
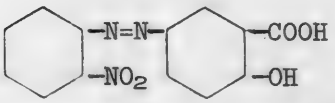
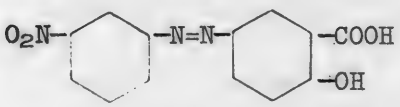
In carrying out these reactions, we used the method of comparison of test samples in the dry state [12]. Color reactions observed on the dry residues may be considered to be of the solid phase type described by Kuznetsov [21].

The reactions were carried out as follows: to 1-2 drops of 1% tungstate contained in a porcelain crucible were added 1 drop of reagent solution, 1-2 drops of a 2N sodium hydroxide, and 3-4 drops of 2N hydrochloric acid. The solutions were mixed and evaporated to dryness on a sand bath. The color of the dry residue was compared with a control

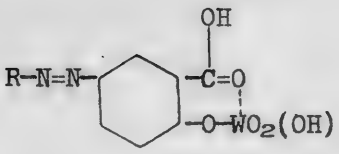
Results are given in Table 1 for five azo dyes – salicylic acid derivatives – which showed the highest sensitivity for tungstates.

TABLE 1

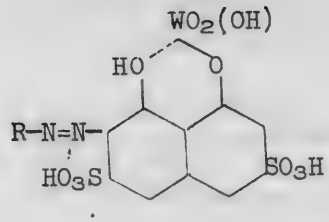
Reactions of Certain Azo Dyes – Derivatives of Salicylic Acid – with Tungstates

Reagent	Color of dry residue		Sensitivity	
	Control test	Test with WO_4^{2-}	Limit of identification, γW in 1 ml	Limiting concentration
	Pale rose-yellow	Bright orange-red	3	1:10000
	Pale yellow	Bright red	3	1:10000
	Pale yellow	Rose-red	6	1:5000
	Pale rose-yellow	Orange-red	30	1:1000
	Pale yellow	Orange-red	30	1:1000

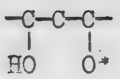
The underlying chemistry of the reactions considered is probably the formation of inner complex esters (IV, V) with a six membered heterocyclic ring; the reaction is determined by the presence of a specific atomic grouping (VI), which is common to both chromotropic and salicylic acids



(IV)



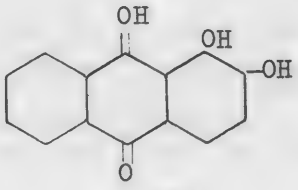
(V)



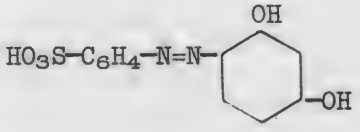
(VI)

where O* is the oxygen atom which forms a coordinate bond.

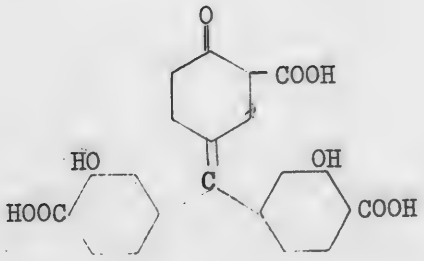
If this assumption is correct, then other organic compounds of different classes but containing this specific grouping should interact with tungstates. Among those compounds which contain this grouping, we tested: alizarin [1,2-dihydroxyanthraquinone (VII)], the azo dye, Tropeolin "O" [sodium salt of sulfobenzeneazoresorcinol (VIII)], and aluminon [ammonium salt of aurine tricarboxylic acid (IX)]. In addition the oxime [8-hydroxyquinoline (X)] was tested.



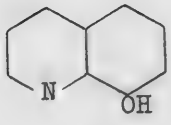
(VII)



(VIII)



(IX)



(X)

Results are given in Table 2.

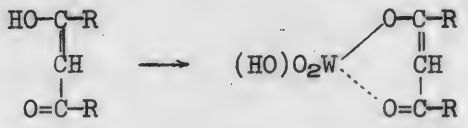
TABLE 2

Reactions of Tungstates with Certain Organic Compounds

Reagent	Color of dry residue	
	Control test	Test with WO_4^{2-}
Alizarin	Pale yellow	Yellow brown
Tropeolin "O"	Pale yellow	Greenish yellow
Aluminon	Rose	Bright orange-red
Oxime	Colorless	Yellow brown

These results show that all these compounds in fact give a color reaction with tungstates.

This same atomic grouping enters into the composition of curcumin (XI), the chemistry of the reaction of which with tungstates has not been hitherto considered [15]. The chemistry of this reaction can now be explained on the basis of the viewpoint developed by us:



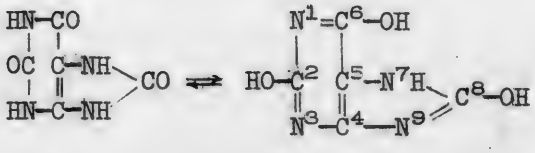
(XI)

where R = $CH{=}CH{-}C_6H_3(OCH_3)OH$.

It is known from Korenman's work [22, 23] on the theory of specific atomic groupings that the oxygen atom which forms the coordinate bond can be replaced by a nitrogen atom. Moreover, one of the carbon atoms which make up the specific grouping can be removed without loss of reactivity. If this is taken into account, the six membered heterocyclic ring can be converted into a five membered ring. It is then possible to do something which has not been attempted before; viz., clear up the chemistry of the reactions of tungstates with pyrocatechol [13] (I), α-benzoinoxime [17] (XII), uric acid [16] (XIII), for which the tautomeric form – 2,6,8-trihydroxypurine, is possible – and 8-hydroxyquinoline.

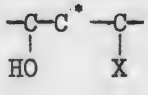
(XII)

(XIV)



(XIII)

(XV)

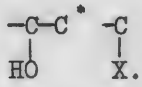


(XVI)

on the basis that the atomic groupings (XIV) and (XV) are special cases of a more general grouping (XVI), where X is the atom of oxygen or nitrogen forming the coordinate bond, and C* denotes the carbon atom, removal of which does not lead to loss of reactivity.

SUMMARY

1. A specific atomic grouping for tungstates has been found in some organic reagents –



The carbon atoms forming the group may occur in both aliphatic and cyclic compounds.

2. It has been shown that organic compounds of different classes containing the specific group indicated can give reactions with tungstates.

3. The underlying reaction is apparently the formation of five or six membered heterocyclic inner complex esters of tungstic acid.

4. The hypothesis developed explains the underlying chemistry of reactions which have been described previously between tungstates and curcumin, azo dyes – pyrocatechol derivatives, α-benzoinoxime, and uric acid.

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QUANTITATIVE DETERMINATION OF TIN WITH ARSONIC ACIDS

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Results of a study of the precipitation conditions of tin by aromatic arsenic compounds have shown that p-hydroxyphenylarsonic acid precipitates tin from acid solutions in the form of difficultly soluble tin p-hydroxyphenylarsonate [1]. This fact has served us as a basis for developing a volumetric method of determining tin. In recent years several papers have been published on the quantitative determination of tin by means of phenylarsonic acid. Knapper, Craig, and Chandlee [2] suggested phenylarsonic acid as a precipitant for Sn (IV). A series of papers followed in which the possibility of using this acid for the quantitative determination of tin was investigated. Of the papers devoted to this question, mention should be made of those of Syrkomsky and Pilnyak [3], Alimarin and Vezhenkova [4], and Kuznetsov [5]. In the last paper listed, Kuznetsov in considering the reasons for the contradictory results obtained by various authors for the determination of tin by means of phenylarsonic acid, came to the conclusion that during the precipitation of tin by means of this acid, it is essential to have the tin in the form of the chloride of metastannic acid since the behavior of the α- and β-compounds of Sn (IV) toward this acid is different. In examining this fact more closely the author exhaustively studied the gravimetric determination of tin by means of phenylarsonic acid.

None of these authors posed the problem of volumetric determination of tin.

We came up against this point during a study of the possible application of various arsonic acids in chemical analysis. Our main object was to develop more rapid analytical methods, and naturally we turned to volumetric methods.

As pointed out already during a study of precipitation conditions of various cations by phenylarsonic acid and some of its derivatives, it turned out that p-hydroxyphenylarsonic acid precipitates tin and certain other elements from mineral acid media. The overwhelming majority of cations are not precipitated under these conditions just as in the case with phenylarsonic acid itself.

Preliminary tests carried out in order to determine optimum precipitation conditions showed that at acid concentrations where most elements are not precipitated at all[1)], tin is practically completely precipitated.

Precipitation of Quadrivalent Tin

A few drops of hydrogen peroxide are added to the test solution which contains ca. 0.001 g Sn per ml, and the solution heated for 10 minutes. On cooling, precipitation is effected by means of 5% sodium p-hydroxyphenylarsonate. The precipitant is added in a one and a half excess.

After addition of all the precipitant an equal volume of water is added and the whole heated for half an hour on a boiling water bath. After cooling the precipitate is filtered off and washed 2-3 times with water.

Analysis of the tin p-hydroxyphenylarsonate thus prepared indicated the following composition:

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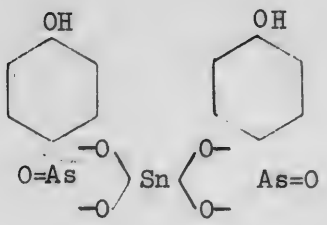
1) Salts of copper, zinc, and lead, etc., are not precipitated.



Method of Treating the Precipitate of Tin p-Hydroxyphenylarsonate

First variant. The washed precipitate of tin p-hydroxyphenylarsonate is dissolved in 10% ammonia. The solution is placed in a standard flask and made up to the respective volume. 20-25 ml of the solution is transferred to a 200-250 ml flask with a ground glass neck, and hydrochloric acid is added in such amount that the acid concentration will be 1-2 N; 0.5 g of potassium bromide and excess of 0.1N $KBrO_3$ are then added and the solution allowed to stand for 15 minutes with frequent shaking. The hydroxyphenylarsonic acid is thereby converted into a tribomophenol.

When bromination is complete 0.1N As_2O_3 is added, and excess titrated against the same solution of $KBrO_3$ used previously, using indigocarmine as indicator. 1 ml of 1N $KBrO_3$ = 0.459 g tin p-hydroxyphenylarsonate or 0.009894 g Sn.

Second variant. This variant differs from the first only in that the tin p-hydroxyphenylarsonate after precipitation and washing is dissolved in concentrated hydrochloric acid by warming on a water bath. In this method, therefore, the filter plus precipitate are transferred to a flask fitted with a ground glass stopper, concentrated hydrochloric acid[1] added, and the solution heated on a water bath until complete solution of the precipitate is effected. Subsequent operations are the same as for the first variant. Results of tin determinations by the two variants are given in Table 1.

TABLE 1

Amount of tin in 1 ml solution, in g	1st Variant			2nd Variant	
	Amount of tin p-hydroxyphenylarsonate			Amount of tin p-hydroxyphenylarsonate	
	Taken, in g	Found, in g	Difference, taken − found, in g	Found, in g	Difference, taken − found, in g
0.001395	0.06474	0.06452	− 0.00022	0.06496	+ 0.00022
0.001395	0.06474	0.06463	− 0.00011	0.06474	0.00000
0.001395	0.06474	0.06474	0.00000	0.06485	+ 0.00011
0.001395	0.06474	0.06452	− 0.00022	0.06474	0.00000
0.001395	0.06474	0.06474	0.00000	0.06485	+ 0.00011
0.001395	0.06474	0.06452	− 0.00022	0.06463	− 0.00011
0.001395	0.06474	0.06474	0.00000	0.06474	0.00000

Note. In all the experiments (Tables 1, 2, and 3), the amount of tin solution to be titrated was 10 ml.

The results given in Table 1 show that both variants give good results even for fairly small amounts of tin in the test solution.

[1] 5N acid may be used if heating is carried on for half an hour.

Table 2 contains results of the determination of tin by the same method but with the difference that the acid concentration in the solution to be titrated was made up to 0.5% while the tin concentration was lowered to 0.00109 g.

TABLE 2

Amount of tin in 1 ml solution, in g	Amount of tin p-hydroxyphenylarsonate		
	Taken, in g	Found, in g	Difference, taken − found, in g
0.00109	0.0506	0.0505	− 0.0001
0.00109	0.0506	0.0504	− 0.0002
0.00109	0.0506	0.0505	− 0.0001
0.00109	0.0506	0.0506	− 0.0000
0.00109	0.0506	0.0504	− 0.0002
0.00109	0.0506	0.0505	− 0.0001

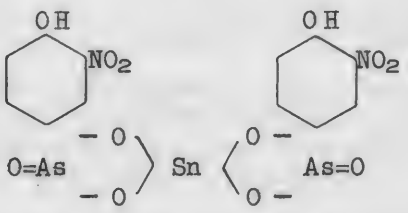
The results in Table 2 show that for 0.5% acid in the test solution, the results are even more accurate. This fact should make it possible to determine tin in the presence of other elements whose arsonates are soluble at that acid concentration.

One of the drawbacks of the method described is the necessity of heating the precipitate for a long time with concentrated hydrochloric acid to dissolve it. The use of ammonia as a solvent (first variant) has the disadvantage that bromination occurs in a heterogeneous medium, which is not convenient. In trying to get a more rational method for the determination of tin, we used p-hydroxy-m-nitrophenylarsonic acid (the uni-sodium salt of p-hydroxy-m-nitrophenylarsonic acid) instead of sodium p-hydroxyphenylarsonate in the following experiments.

Determination of Tin by Means of Sodium p-hydroxy-m-nitrophenylarsonate

The solution of tin to be analyzed is prepared as for determination by means of sodium p-hydroxyphenylarsonate. A threefold excess of precipitant is used (a 5% aqueous solution of sodium p-hydroxy-m-nitrophenylarsonate). As soon as the precipitant is added, a precipitate of tin p-hydroxy-m-nitrophenylarsonate, which is of a light cream color, forms.[1])

Analysis of the precipitate indicates the following formula for tin p-hydroxy-m-nitrophenylarsonate:



The precipitate is allowed to stand in the solution for 1 hour. At the end of this time, it is filtered and then washed on the filter 5-6 times with water or 2-3 times with 1N hydrochloric acid. After washing, precipitate and filter are placed in a wide necked flask and 25 ml of 2N hydrochloric acid added, the mixture is heated on a water bath until the precipitate has dissolved completely (30 minutes). This solution is transferred to a 100 ml standard flask and diluted to the mark with 2N hydrochloric acid.

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1) When there is even only 4μ g of Sn in 1 ml of solution, the formation of a precipitate by addition of p-hydroxy-m-nitrophenylarsonic acid and p-hydroxyphenylarsonic acid is still fairly easily observable.

20-25 ml of solution is taken for each determination. Conditions for bromometric determination are the same as for determination by means of sodium p-hydroxyphenylarsonate. The only difference is that on bromination of p-hydroxy-m-nitrophenylarsonic acid the dibromo derivative is obtained. (The equivalent weight of tin p-hydroxy-m-nitrophenylarsonate is M/8). Results of tin determinations by this method are given in Table 3.

TABLE 3

Amount of tin in 1 ml of solution, in g	Tin found, in g	Difference, taken − found, in g	Observations
0.00198	0.0199	+ 0.0001	Starting with the fifth experiment, the acid concentration in the test solution was made up to 1%.
0.00198	0.0198	0.0000	
0.00198	0.0196	− 0.0002	
0.00198	0.0196	− 0.0002	
0.00218	0.0216	− 0.0002	
0.00218	0.0218	0.0000	
0.00218	0.0216	− 0.0002	
0.00218	0.0217	− 0.0001	

The results of this last series of tests indicate that determination of tin by means of sodium p-hydroxy-m-nitrophenylarsonate is fairly accurate even for a concentration of 1% acid in the test solution and has the following advantages over the method involving sodium p-hydroxyphenylarsonate as precipitant:

1) tin p-hydroxy-m-nitrophenylarsonate does not require heating for precipitation;

2) tin p-hydroxy-m-nitrophenylarsonate dissolves comparatively easily on heating in 2N HCl, so that there is no need to heat it in concentrated hydrochloric acid (which is one of the drawbacks of the method involving sodium p-hydroxyphenylarsonate);

3) the precipitate of tin p-hydroxy-m-nitrophenylarsonate is easier to handle during all the operations than that of tin p-hydroxyphenylarsonate.

SUMMARY

1. New methods have been worked out for the volumetric determination of tin by means of sodium p-hydroxyphenylarsonate and sodium p-hydroxy-m-nitrophenylarsonate.

2. Of the two methods described the one in which sodium p-hydroxy-m-nitrophenylarsonate is used is the better.

3. Precipitation of tin by sodium p-hydroxy-m-nitrophenylarsonate proceeds quantitatively even for a 1% hydrochloric acid concentration in the test solution. This may be taken advantage of for working out a method of determining tin in the presence of a number of other metals which often accompany tin.

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CHRONICLE

Nikolai Aleksandrovich Tananaev

(On his 75th birthday)

This year the Chemical Society of our country celebrates the 75th birthday and the 45th year of scientific and teaching activity of one of the oldest analytical chemists, a Stalin Laureate, and a doctor of chemical sciences, Professor Nikolai Aleksandrovich Tananaev.

The development of Soviet analytical chemistry during the last 30 years has been closely connected with the name of Tananaev, who is one of the outstanding scientists in this branch of chemistry.

Spot analysis, which was first developed by Tananaev in the Soviet Union, has now been widely developed. This method is of great practical importance. Special reactions proposed by Tananaev and the systematic system of analysis based on these reactions, as well as the new method of "in situ analysis" are of great value in analytical chemistry.

N. A. Tananaev has always followed new paths in his scientific and teaching activities, as a result of which he has worked out new methods of chemical analysis and written original text books in analytical chemistry, such as "Spot Tests," "Special Reactions and a Systematic Analysis Based on Them," and "In Situ Analysis."

Tananaev has paid a lot of attention to volumetric and gravimetric analysis, and in these fields he has carried out many investigations. On his own, and in conjunction with his students, he has published ca. 200 papers.

Of particular value in Tananaev's scientific research activity is the intimate relation between theory and practice.

N. A. Tananaev is a wonderful teacher who has educated many cadres of analytical chemists and many of his pupils have turned out to be leading specialists in this branch of chemistry. His books "Volumetric Analysis," "Gravimetric Analysis," and "Analytical Chemistry," have been text books for a whole generation of analytical chemists. These books have played an important part in making analytical chemistry an independent subject.

His activities have been rewarded with awards and prizes by the Soviet Government. He has received the following awards: Order of Lenin, Order of Merit, A Medal for Work in the Great War, and A Medal for Ferrous Metallurgy. N. A. Tananaev received a Stalin Prize for his work on "In Situ Methods."

The Editorial Board of the Journal of Analytical Chemistry and a wide circle of Soviet analytical chemists, friends, and scientists wish Nikolai Aleksandrovich the best of health, and further successes in his work for the good of our country.

Izrail Mironovich Korenman

(On his 50th birthday)

During January 1954 Izrail Mironovich Korenman who is a professor, a doctor of chemical sciences, and head of the chair of Analytical Chemistry in Gorky State University, celebrated his 50th birthday and his 25th year of activity as a scientist and teacher.

After finishing his course in the Odessa Chemico-Pharmaceutical Institute and getting his degree, Korenman was made a lecturer. Since 1937 he has been the head of the Analytical Section in Gorky State University. In 1940 he was made professor.

To date Korenman has published 230 papers including 5 monographs. He carried out his first scientific research during his student days. While still a candidate for his degree, he prepared a monograph on microcrystalloscopy which was issued in 1931 and was the first Soviet text book on this branch of analytical chemistry. He has successfully worked on the development of micro- and ultra-microchemical analysis; he has written a valuable text book· "Quantitative Microchemical Analysis."

Korenman has devoted considerable energy to working out and improving methods in sanitation and hygiene analysis. Some of the methods which have been worked out with his participation and the instructions drawn up on the basis of these methods have in no little degree contributed to improving the conditions of work in industrial enterprises. He started to work in organizations dealing with this type of work as long ago as 1928, and still continues to work with them.

In recent years Korenman has published many papers on the theory and practice of organic analytical reagents, in particular, on the development of views on so-called characteristic atomic groupings; the idea of "cyclic groupings" is his, these being the skeletal structures of characteristic groupings. He has described quite a few new color and microcrystalloscopic reactions with organic reagents for various elements. Korenman has described original flotation reactions for a large number of elements, whereby the selectivity and sensitivity of the basic reactions on which they are based can be increased considerably.

He has also been attracted to physico-chemical methods of analysis, and various physico-chemical researches: determination of the instability constants of complex ions, questions of the color of precipitates, questions of solubility, etc. He has also been occupied recently with the question of coprecipitation which is of very great importance in contemporary analytical chemistry.

Not only is he a foremost scientist, but he takes an active part in social life. He initiated and organized the conference on analytical chemistry held at Gorky State University in 1952.

As an active member of the Russian Communist Party (from 1941), he has carried out social work in Gorky University, and heads the philosophy seminary in the House of Science. In 1951 he was awarded the Order of the Red Banner of Labor.

We wish Korenman who is celebrating his birthday the best of health and many, many years of fruitful work for the glory of our great country.

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